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APPLIED SPECTROSCOPY

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The Quantitative Determination of Gallium in Micro Samples by the Graphite Spark

E. M. Murt and J. C. Bready

Philco Corporation, Lansdale Division, Lansdale, Pa.

Abstract

A quantitative spectrographic procedure is described for the determination of gallium in micro samples of indium-gallium alloys. A solution procedure is employed with spark excitation and molybdenum as the internal standard. The accuracy of the method ranges from 11% to 22% depending on the concentration level of interest.

Introduction

The field of transistor production and development is continually posing unique analytical problems to chemists concerned with the quality control of incoming materials. Recently this laboratory had been requested to analyze a number of micro samples of indium-gallium alloys for gallium. The largest sample weighed 0.4 mg. It is not desirable nor always possible to consolidate these small samples into one large sample and then analyze it for gallium. Valuable information often can be obtained by the determination of the gallium content in one indium-gallium pellet or sphere. The gallium concentrations in these indium-gallium alloys range from 0.1% to 1.2%.

Onishi *(1)* reported a wet chemical method for the determination of gallium at the millimicrogram level. Murt *(2)* detected gallium at the 50 millimicrogram level, but this was not considered a quantitative procedure. Hyman *(3)* in his recent article thoroughly reviewed many of the possible spectrographic procedures for the quality control of low concentration elements in indium alloys. The porous cup procedure for the quality control of indium alloys used in transistor fabrication applied very well when large (40 mg) samples were available. Baer and Hodge *(4)* in their investigation of spectrochemical solution techniques have pointed out that the small amount of sample required is one of the advantages of the use of the flat top electrode for solution analysis.

Fred, Nachtrieb, and Tomkins *(5)* previously reported high sensitivities using a copper spark method in which 0.1 ml of a HCl solution of the sample is evaporated on the ends of flat-topped copper electrodes.

Morris and Pink *(6)* recently reported excellent sensitivities in the determination of Group III (Boron, Aluminum, Gallium, and Indium) and Group V (Phosphorous, Arsenic, and Antimony) elements at the millimicrogram level using a graphite spark method in conjunction with a chemical pre-concentration step.

As a result of examining the literature, it was decided that the sensitivity and precision of the graphite spark technique provided a good basis for the analysis of the micro samples of interest. This paper describes the procedure developed for the determination of gallium in micro samples of indium-gallium alloys by the graphite spark technique with molybdenum as the internal standard.

Experimental

Method

A HCl solution of the sample is prepared. The flat end of the graphite electrode is coated with Apiezon *N*[†] solution. The molybdenum internal standard and the sample solution are pipetted onto the surface of the upper and lower electrodes and dried. The high voltage spark is used for excitation and the spectra are recorded photographically. The intensity ratio of the gallium analytical line and the internal standard molybdenum line are determined photometrically, and the concentration of the gallium is read from an analytical curve relating log intensity ratio to log concentration. The apparatus and operating conditions are listed in Table I.

Standards

The standard indium solution (2 mg/ml) was prepared by dissolving 200 mg of high purity indium in 100 ml of 12 *N* HCl, and the gallium solution (0.1 mg/ml) was prepared by dissolving 10 mg of high purity gallium in 100 ml of 12 *N* HCl. The standard molybdenum solution was prepared by dissolving ammonium molybdate in distilled water to give a concentration of 0.005 mg molybdenum/ml.

These indium and gallium standards were used to prepare solutions having a gallium concentration ranging from 0.1 to 1.2% based on 0.100 mg of indium-gallium alloy

---

[†] James G. Biddle Co., Philadelphia, Pa.

TABLE I. APPARATUS AND OPERATING CONDITIONS

Spectrograph	Bausch and Lomb Large Littrow Prism
Slith width μ	30
Distance, slit-source, in.	24
Aperature at collimator, mm	16
Slit height, mm	1.5
Range, A	2490-3470
Electrodes	Graphite with flat end
Diam., in.	0.180
Length, in.	1.5
Excitation Unit	National Spectrographic Laboratories Spec Power
Analytical gap, mm	2
Auxiliary gap, mm	2
Output voltage, v	8000
Capacitance, μf	0.005
Inductance, mh	0.600
Secondary resistance, ohm	3
Discharges/half cycle	7
Film	Kodak Spectrum Analysis 103-0 plate
Processor[a]	National Spectrographic Laboratories Plate Processor
Exposure, sec	20
Microphotometer	Jarrell-Ash Non-recordingMicro-photometer

[a] Processed according to standard procedures (7,E 115-56T).

per 1.0 ml of solution. The final concentration of the HCl solution containing the indium-gallium standards was kept between 1 *N* and 2 *N*.

Sampling

Micro samples of indium-gallium alloys were weighed on a precision micro balance* and then transferred to a 1-ml volumetric flask. Then, 0.1-0.3 ml of 8 *N* HCl was added and heated to 90-100°C until the alloy was completely dissolved. The final acid concentration should be between 1 and 2 *N* and thus conform to the standard solution concentration. This was obtained by diluting the 8 *N* HCl containing the alloy with distilled water and 1 *N* HCl in order to give a final alloy concentration of 0.100 mg/1.0 ml. For example, if one sample weighed 0.056 mg, this would require a total volume of 0.56 ml to give the required alloy concentration. The sample was dissolved in 0.15 ml of 8 *N* HCl and diluted with 0.41 ml of distilled water.

Two drops of Apiezon-ether solution (5 g Apiezon N/l petroleum ether†) were added to both the upper and lower electrodes. After these had dried, 0.05 ml of the standard molybdenum solution was delivered to both electrodes. An infrared heating lamp was used in the drying of the electrode. After the molybdenum solution had dried, 0.05 ml of the solution to be analyzed was added to both electrodes and dried. Samples which weighed 0.090 mg or more were normally run in quadruplicate. The samples were then sparked within 30 min after they had been prepared on the electrodes. Care should be exercised to avoid excessive heat in drying the samples and thus eliminate any spattering of the solution on the electrode surface. The samples were kept under the heating lamp until they were ready to be sparked to avoid absorption of moisture on the electrode surface.

After the electrodes had been sparked, they were resurfaced on a lathe and could be reused.

Determination of Analytical Curve

Transmittance of the spectrum line pair gallium 2874.2 A and molybdenum 2879 A were determined with a nonrecording microphotometer. These transmission values were converted to relative intensities using an emulsion calibration curve obtained in accordance with recommended procedures (*7*, E 116-56T). From the data obtained on 5 indium-gallium standards containing 0.1, 0.2, 0.6, 1.0, and 1.2% gallium, a working curve (Figure 1) was plotted on two cycle log-log graph paper relating the concentration of gallium to the intensity ratio of gallium 2974.2 A to molybdenum 2879 A. A straight line relationship was obtained by sparking the synthetic standards in triplicate. The average intensity ratio value for the 1.0% gallium falls below the working curve. It is believed that the hydrochloric acid might have possibly penetrated the Apiezon coated electrodes here and caused a variation in line intensity ratios.

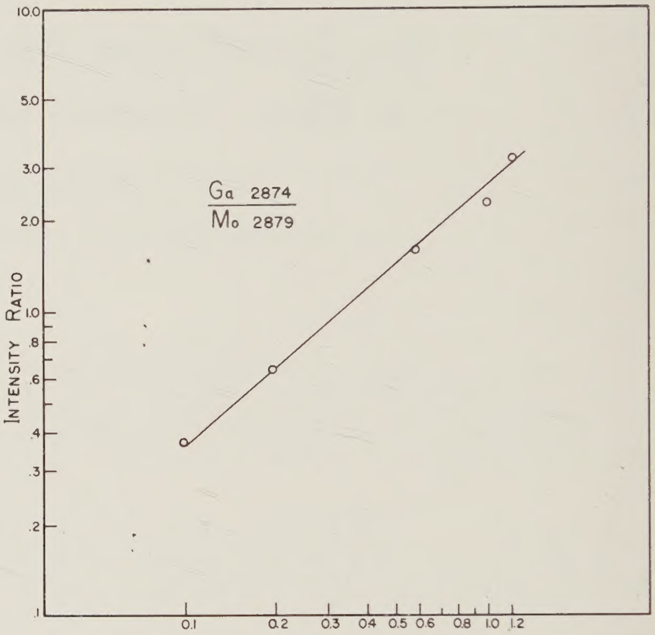

FIG. 1. WORKING CURVE

Precision and Accuracy

Normally the accuracy of a spectrographic procedure is evaluated by comparison with wet chemical or other analytical results. A comparison of results for gallium and the wet chemical method of Onishi *(1)* would necessitate a complete evaluation of the chemical procedure for its reliability at these concentrations in an indium matrix. Since this information was not available, data were obtained which indicated the expected precision and accuracy of the spectrographic method (Table II). The three synthetic solution standards used to obtain this information represented alloys containing 0.2%, 0.6%, and 1.0% gallium. Ten exposures of each standard were made and the concentration values were obtained from the previously prepared analytical curve.

TABLE II. PRECISION AND ACCURACY DATA[a]

Gallium Concentration	*Standard Deviation from Ga Added*	*Coefficient of Variation*
0.200	±0.044	±22
0.600	±0.078	±13
1.00	±0.11	±11

[a] All values in percent.

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*August Sauter Inc., New York, N. Y.

†Petroleum ether, Certified, A.C.S., b.p. 30-60°, sp. gr. 0.625-0.650/25°

Discussion

The described method is ideally suited for the determination of minor concentrations of gallium in indium-gallium alloy micro samples. This procedure provides for rapid analysis, versatility, and satisfactory accuracy for the needs of this control program at the present time. Normally one sample of alloy can be processed in quadruplicate in 3 hr. It is possible to run 9 determinations on a 0.100 mg sample.

Molybdenum is used as an internal standard since it has been found to provide satisfactory reproducibility and a large number of available reference lines.

It is believed the accuracy and precision could be improved by use of an electrode coating which is more impervious to hydrochloric acid. Investigation is also being carried on to evaluate the increased sensitivity that can be obtained by using gallium lines 4032.9A and 4172.1A and sparking the samples in a controlled atmosphere.

Since some electrical characteristics of certain types of transistors are dependent on the amount of gallium present in the individual dot that is used in fabricating the transistor, this procedure offers a means of checking individual indium-gallium dots even though they weigh considerably less than 0.1 mg. This technique can aid in the study of segregation effects and processing variables and is extremely useful when sample size is limited.

This method is considered satisfactory for the routine analysis of micro samples of indium-gallium alloys. It has also found wide application in the analysis of micro amounts of indium-gallium alloys which have been electroplated on small diameter wire.

Acknowledgment

The authors wish to acknowledge Mr. T. Manns for his encouragement in this work and Miss S. Gross for her assistance in evaluating this method.

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(1) H. Onishi, Anal. Chem. **27,** 832 (1955)

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(5) M. Fred, N. H. Nachtrieb, and F. S. Tomkins, J. Opt. Soc. Am. **37,** 279 (1947)

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(7) *Methods for Emission Spectrochemical Analysis*, Am. Soc. Testing Materials, Philadelphia, Pa., 1957

Submitted November 23, 1959

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The Spectrographic Determination of Uranium 235. Part II. Using a Direct-Reading Attachment and a Hollow Cathode Source†

Ted Lee and Lewis H. Rogers

Technical Division, Oak Ridge Gaseous Diffusion Plant,
Union Carbide Nuclear Company, Oak Ridge, Tennessee

Abstract

This report, the second of a series associated with the development of the spectrographic determination of U^{235} at the Oak Ridge Gaseous Diffusion Plant, describes the development of the direct-reading scanning technique, using a Jarrell-Ash 21-foot Wadsworth spectrograph with a hollow cathode discharge tube to excite the uranium samples. For a determination consisting of ten scans on a single cathode containing the unknown, and ten scans on a single cathode containing a comparison standard, the precision obtained was from ±1.2 to 1.8% of the amount present over a concentration range of 8-12% U^{235}. All precisions are expressed at the 95% confidence level.

Introduction

This report presents an evaluation of a direct-reading scanning technique for isotopic assay of U^{235} for the range from 8 to 12% using a hollow cathode discharge tube and a direct-reading attachment on a Jarrell-Ash Wadsworth spectrograph. An estimate of the precision at other concentrations may be made by comparing the present evaluation with that in Part I (*1*) of this series. That report covers the concentration range from the level of naturally occurring uranium to over 90% U^{235} using the same spectrograph with dc arc excitation and photographic recording. Precisions were limited by the available resolution and dispersion of the spectrograph. Although special instruments are available with high resolution and dispersion, the method described in this paper remains attractive for laboratories with limited facilities. The speed and precision of direct-reading measurements makes the method potentially useful for routine applications and as a supplement to mass spectrometry and fission counting.

The scanning technique alone was selected for evaluation, since a preliminary examination showed that the integration technique adopted from developments by Hassler, Lindhurst, and Kemp (*2*) and Saunderson, Coldecourt, and Peterson (*3*) was not feasible with the available resolution. The integration technique involves precise positioning of three exit slits and photomultiplier tubes over the U^{235} line, a non-isotopic uranium line, and a relatively clear region for background measurements. The very dense background, the closeness of the isotopic lines, and the limited resolution available did not permit maintaining the precise exit slit alignment needed for the integration method.

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†This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission. The experimental work was completed July 31, 1951 and declassified February 29, 1956.

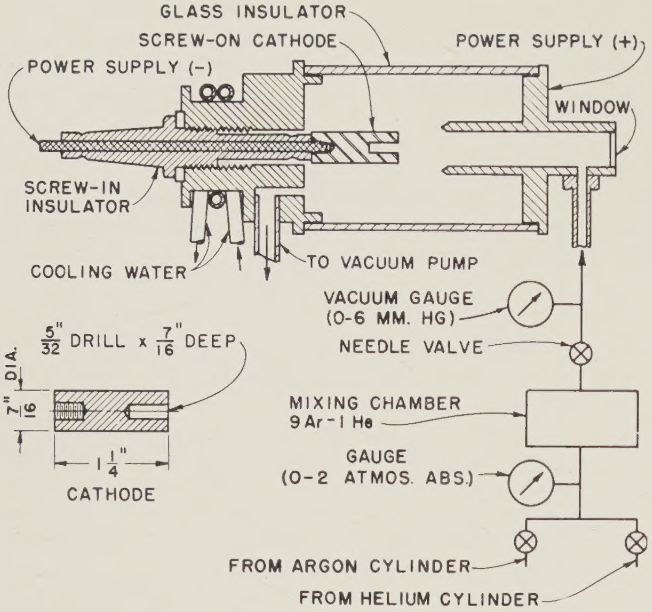


FIG. 1. HOLLOW CATHODE SOURCE AND GAS MIXING SYSTEM

The direct-reading scanning techniques are based on developments by Dieke (*4*), and Crosswhite (*5*), and Brody, Tomkins, and Fred (*6-8*), who first successfully combined a hollow cathode discharge lamp with photomultiplier tubes and electronic recording to measure directly the intensities of the isotopic uranium lines. The isotopic displacement effect in uranium spectra used in this evaluation was reported by Long and Smith (*9*) in 1947. Other investigators in this field are cited in a previous report (*1*).

Experimental

Hollow Cathode Discharge Tube

A hollow cathode discharge tube was used as an excitation source because of its stability, production of narrow spectral lines, economy of sample, and long life. The tube was designed by McNally; a prototype was described by McNally, Harrison, and Rowe (*10*). The tube and gas flow system are shown in Figure 1. The hollow cathode source was excited at 100 milliamp through a 2000 ohm ballast resistor by a dc power supply of conventional design. The power to the hollow cathode source was controlled with a Variac in the primary of the high voltage transformer. Any dc power supply capable of delivering the required current at about 600 volts, to ionize the support gas, may be used. Since only an initial optical alignment of the hollow cathode source was necessary, this was available by attaching the source to the end of a Jarrell-Ash lens support which permitted all required degrees of adjustment.

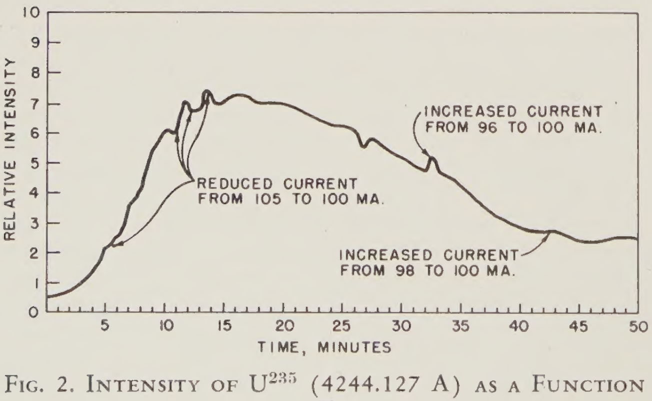
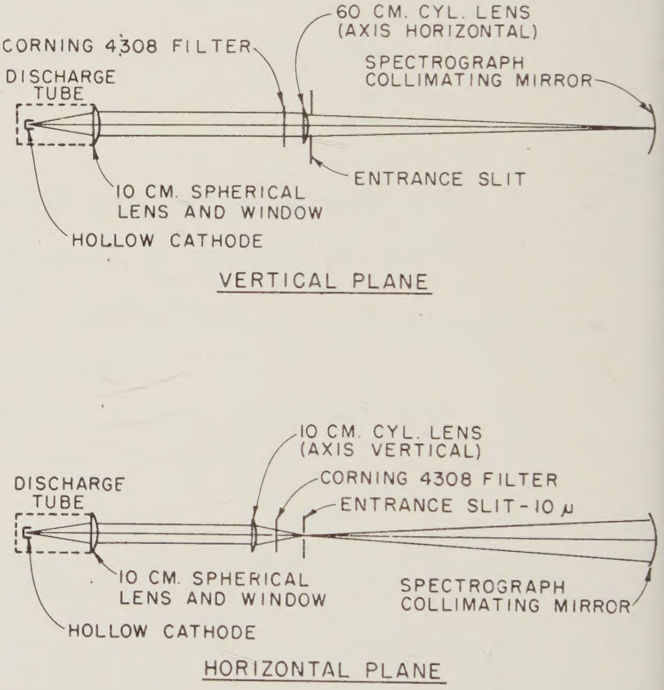


FIG. 2. INTENSITY OF U^{235} (4244.127 A) AS A FUNCTION OF TIME

The uranium samples were prepared for excitation by transferring to the cavity of an iron cathode a few drops of uranyl nitrate solution containing 4 mg of $UO_2(NO_3)_2$ and evaporating to dryness. Loose particles were removed by inverting and tapping the cathode before inserting into the lamp. Direct excitation of dry U_3O_8 samples was unsatisfactory, since the oxide particles caused instability, and required several hr preburn before a stable signal could be obtained.

Sputtering-gas mixtures of 1:2, 1:1, 2:1, 4:1, 9:1, and 19:1 mole parts of argon to helium, as well as pure argon and pure helium, were investigated. Maximum intensity of the uranium spectrum was obtained with a mixture of 9 parts argon to 1 part helium at a pressure of 3 mm Hg absolute, as recommended by Brody.

A recording of the U^{235} intensity as a function of time, showing the build up and decay of the signal from the hollow cathode source, is shown in Figure 2. This recording indicates a rapid build up of intensity during the first 15 min, after which the intensity levels off and then decreases slowly. Intensity measurements on samples were, therefore, made after the 15-min build up period.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SPECTROGRAPH COLLIMATING MIRROR
HOLLOW CATHODE
HORIZONTAL PLANE

FIG. 3. OPTICAL SYSTEM USED WITH THE JARRELL-ASH SPECTROGRAPH

Spectrograph

A Jarrell-Ash Wadsworth spectrograph, with a 5 in. diam. grating ruled with 15,000 lines/in. and having a 21-ft radius of curvature was used in the second order to provide a theoretical resolution of 150,000 and an inverse linear dispersion of 2.5 A/mm. The optical system is shown in Figure 3. The entrance slit was 10 μ wide and 15 mm high. The radiation from the source was made parallel by using a 10 cm spherical lens, which also served as the window for the discharge tube. Crossed cylindrical lenses, as used by G. Hansen and described by Harrison, Lord, and Loofbourow (*11*), were applied as follows: a 10 cm cylindrical lens (axis vertical) was used to focus, in the horizontal plane, the parallel light on the slit; a 60 cm cylindrical lens (axis horizontal) was used to focus the light on the collimating mirror. With this arrangement, a narrow beam of light was produced along the length of the entrance slit, and most of the light that passed through the entrance slit fell on the collimating mirror. Although relatively uniform slit illumination was provided, this is not a requirement for direct-reading measurements. The glass filter (Corning No. 4308) removed interference from other orders.

Direct-Reading Scanning Technique

A single 50 μ exit slit and a 1P21 photomultiplier tube in a light-tight metal housing, similar to that described by Brody (*6-8*), Crosswhite (*5*), and Dieke (*4*), was mounted in place of the conventional photographic plateholder of a Jarrell-Ash spectrograph to measure the intensities of the isotopic uranium lines at 4244 A. In the Jarrell-Ash instrument (*12*), the grating is mounted permanently at right angles to the axis of a long bar. The plateholder (or direct-reading measuring unit) is maintained on the grating normal by locating it at the far end of this bar. With the angle of reflection thus established, the spectral region is changed by varying the angle of incidence, rotating the bar and the grating about a pivot centered under the grating face. A scanning drive was devised, consisting of a ⅓ rph (2 deg/min) motor coupled to the bar with an eccentric bearing and connecting rod. The eccentricity was 0.344 in. The rotatory motion of the motor shaft is thus converted to a reciprocating motion transmitted to the bar which, in effect, moves the exit slit and photomultiplier tube across the spectrum at approximately 0.2 mm/min. Using the isotopic uranium lines at 4244 A, 30 sec were required to scan from the U^{238} peak at 4244.373 A to the U^{235} peak at 4244.122 A and an additional 15 sec to scan from the U^{235} peak to the region selected for background measurements at approximately 4244.0 A.

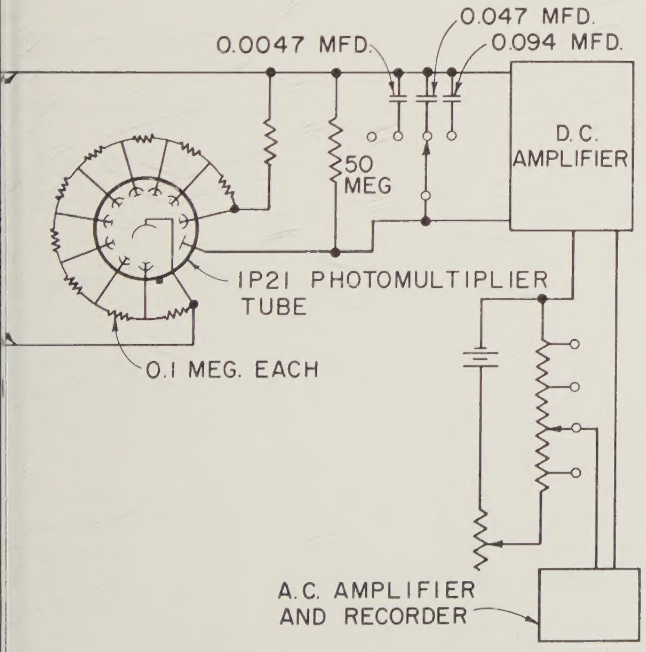

FIG. 4. Simplified Schematic Circuit Diagram for Scanning

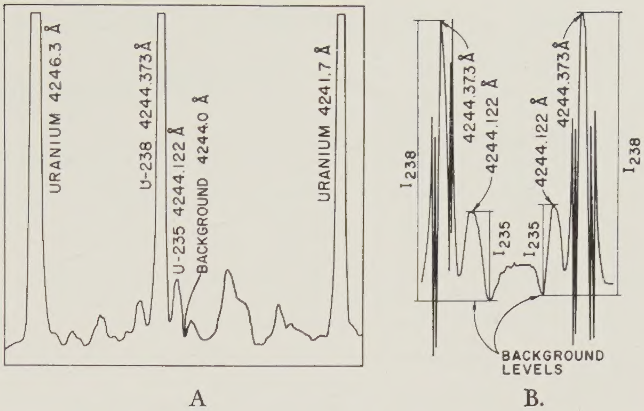

Fig. 5. A—Uranium Spectrum, B—Typical Scanning at 10% U^{235}

The output from the photomultiplier tube was transmitted to a recorder through a 100% negative feed back amplifier (*13*). A simplified schematic diagram of the electronics for scanning is shown in Figure 4. The time constant of the electronics was selected to average out the shorter period fluctuation in the signal current without suppressing the scanning peaks, by switching an appropriate capacitor across the anode load resistor.

A recording of the region from 4241 A to 4246 A is shown in Figure 5A. The U^{235} peak (4244.122 A), the U^{238} peak (4244.373 A), and the region where background was measured (4244.0 A) are indicated. In Figure 5B is shown a recording of a typical measurement of the intensity ratio of U^{235} to U^{238} at the 10% assay level. The amplifier had been adjusted for sufficient sensitivity to record the weaker U^{235} line. The U^{238} line was measured at the same sensitivity by introducing a bucking voltage, to move the recorder pen downscale a calibrated distance. The "shoulders" on each side of the U^{238} line shown in Figure 5B were caused by introduction of and removal of the bucking voltage in equal steps as the exit slit scanned the line.

To obtain the best analytical precision for the 45 sec period required to scan U^{238}, U^{235}, and the background, it was necessary that the absolute intensity remain constant during this period. Examination of Figure 2, which shows a recording of the absolute intensity of U^{235} as a function of time, indicates a slow decay after the 15 min build up. To reduce the effect of this drift, the spectrum was scanned in both directions (Figure 5B), and the average taken as a single measurement. A more precise method to compensate for variation in the absolute intensity might be to use a second photomultiplier tube and exit slit measuring the intensity of a total uranium line, and record the ratio of the outputs of the scanning tube to the reference tube (*4,5*).

Determination of U^{235}

The % U^{235} was determined from the measured intensity ratio of U^{235} to the sum of U^{235} and U^{238}. Direct background corrections were obtained by measuring the U^{235} and U^{238} peaks above the measured background, as indicated on the recording in Figure 5B. Each result is the average of ten repeat scans or measurements on a single cathode. From the average intensity ratio, the % U^{235} in a sample could be determined with a calibration curve or by direct comparison with standard samples.

TABLE I. SCANNING MEASUREMENTS OF U^{235}

Mass Spectrometer Data			*Optical Spectrochemical Data*			
	Precision				*Precision*	
Known % U^{235}	*Absolute (% U^{235})*	*Relative (% of Value)*	*Measured Intensity Ratio*	*Measured % U^{235}*	*Absolute (% U^{235})*	*Relative (% of Value)*
7.962	±0.035	±0.44	0.079 ± 0.001	8.00	±0.14	±1.79
9.860	±0.044	±0.45	0.100 ± 0.001	9.72	±0.12	±1.21
10.366	±0.046	±0.44	0.107 ± 0.002	10.52	±0.17	±1.63
11.903	±0.051	±0.43	0.125 ± 0.001	11.89	±0.19	±1.59

CALIBRATION CURVE. The intensity ratios of the U^{235} to the sum of the U^{235} and U^{238} spectral lines at 4244 A were determined on 4 standards ranging from 8 to 12% U^{235}. A plot of the average intensity ratios (column 4, Table I) as a function of known % U^{235} (column 1, Table I) resulted in an essentially linear working curve.

DIRECT COMPARISON WITH STANDARD SAMPLES. Each of the 4 standards was treated in turn as an unknown to evaluate the precision by a method similar to that employed with mass spectrometry at the Oak Ridge Gaseous Diffusion Plant to determine the % U^{235} in an unknown with a single standard close to the unknown in U^{235} concentration *(14)*. The % U^{235} was determined from the measured intensity ratio of the unknown and of an adjacent standard, and the known % U^{235} in the adjacent standard. The following relationship was applied:

$$\frac{\%\, U_X^{235}}{\%\, U_S^{235}} = \frac{(I_{U^{235}}/I_{U^{235}} + I_{U^{238}})_X}{(I_{U^{235}}/I_{U^{235}} + I_{U^{235}})_S}$$

where I is the intensity measured above background, and X and S represent the unknown and standard. In deriving the above relationship, it was assumed that the mole per cent U^{235} is directly proportional to the measured intensity ratio, an assumption believed valid for the isotopic lines at 4244 A when proper background corrections are made. Minor isotopes (U^{234} at 4244.075 A and U^{236} at 4244.226 A which are present up to a few per cent) could not be resolved, and hence no corrections were made. Any difference in the concentrations of these isotopes between the unknown and standard would introduce a bias. The results obtained and an evaluation of the precision at the 95% confidence level are given in Table I.

Summary and Conclusions

A Jarrell-Ash 21-ft Wadsworth spectrograph with a 5-in. 15,000 line/in. grating, was adapted for direct reading of the isotopic uranium lines by attaching a specially constructed housing containing an exit slit and photomultiplier tube. Using this instrument in the second order and a hollow cathode discharge tube to excite the sample, a series of scanning measurements on samples containing between 8 and 12% U^{235} showed a precision ranging from 1.2 to 1.8% of the amount present, expressed at the 95% confidence level. The precision represents a five-fold improvement over the precision previously obtained with dc arc excitation and photographic recording *(1)*. The precision may have been further improved with an exit slit narrower than the 50 μ used. Although the present technique requires about 10 min exposure time as compared with 1 min using dc arc and photographic recording, the overall effort is less, since subsequent emulsion calibration, photographic processing, and photometric measurements are not required.

Better precision would be expected with presently available spectrographs employing gratings specially blazed for the higher orders to provide higher resolution and dispersion. Laboratories which have no need for more precise determinations, and which have limited facilities, should find the present method attractive.

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Spectroscopic Standard Samples of Titanium and High-Temperature Alloys

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Abstract

Ten new spectroscopic standard samples are now available from the National Bureau of Standards. These consist of three standards each for two titanium alloys and four standards for high-temperature alloys. The new standards are useful for both optical emission and x-ray methods of analysis.

Titanium Alloys

Six new spectroscopic standard samples, for two additional titanium alloys, have been added to the three standards previously made available by the National Bureau of Standards for the titanium alloy, 6 Aluminum - 4 Vanadium type. The alloys, covered by a nominal together with a high and a low composition standard, are: 8 Manganese type and 2 Chromium - 2 Iron - 2 Molybdenum type. An announcement of iron-base standards was made previously by the National Bureau of Standards *(1)*.

Although the use of titanium and its alloys has not reached the level predicted several years ago, there has been a steadily increasing use of this lightweight material primarily in aircraft applications and certain corrosion problems. Accurate and reliable methods of analysis, together with standard samples, are thus required to maintain the composition requirements.

In all, some 27 titanium-base standards are planned for certification, three each for eight principal titanium alloys, and a series of three for unalloyed titanium. The material for the standards was prepared by a triple-arc melting process under vacuum at Armour Research Foundation under contract with the Air Force, Wright Air Development Center. The ingots were processed to rods for standard samples by the Allegheny-Ludlum Steel Corporation.

Preliminary studies of homogeneity were made by Armour Research Foundation, Watertown Arsenal, and Spectrochemical Laboratories Inc., and this was followed by an extensive examination at the National Bureau of Standards. Material was accepted for use as standard samples when the overall variation in composition of the cross section and along the length did not exceed plus or minus one percent of the amount shown to be present by the specific testing employed.

Table I. Spectroscopic Titanium-Base Standards[a]

	Titanium Alloy, 8 Manganese Type (New)		
NBS No.	*641*	*642*	*643*
Designation	*8 Mn, (A)*	*8 Mn, (B)*	*8 Mn, (C)*
Element		*Per Cent*	
Mn	6.6_8	9.0_8	11.6_8
	Titanium Alloy, 2 Chromium - 2 Iron - 2 Molybdenum Type (New)		
NBS No.	*644*	*645*	*646*
Designation	*2Cr-2Fe-2Mo(A)*	*2Cr-2Fe-2Mo(B)*	*2Cr-2Fe-2Mo(C)*
Element		*Per Cent*	
Cr	1.03	1.96	3.43
Fe	1.36	2.07	2.14
Mo	3.61	2.38	1.11
	Titanium Alloy, 6 Aluminum - 4 Vanadium Type[b]		
NBS No.	*653*	*654*	*655*
Designation	*6Al-4V (A)*	*6Al-4V (B)*	*6Al-4V (C)*
Element		*Per Cent*	
Al	7.25	6.03	4.63
V	2.58	3.83	5.38

[a] Size: Disks 1¼-in. in diam. and ¾-in. thick.

[b] Previously made available.

Table II. Compositions of Four New High-Temperature Alloy Spectroscopic Standards[a]

NBS No. *Designation*	*1186* *16-25-6* *(Cr-Ni-Mo)*	*1188* *Inconel "X"* *550*	*1191* *Waspaloy*	*1192* *Waspaloy* *Modified*
Element		*Percent*		
C	0.074	0.035	0.020	0.018
Mn	.72	—[b]	.02	.17
Si	.85	.66	.26	.47
Cr	16.6_0	15.4_0	19.4_8	17.8_8
Ni	24.5_0	72.6_5	55.1_5	57.2_5
Co	(0.05)[c]	—	13.6_5	11.4_0
Mo	5.9_2	(0.3)	4.6_2	7.3_3
W	(<0.01)	(0.02)	(0.05)	(<0.01)
Nb	—	1.11	(<0.01)	(<0.01)
Ti	—	2.14	3.10	2.72
Al	—	0.76	1.55	1.07
Fe	50.7	6.6_0	2.04	1.58
Cu	—	—	0.033	0.056
Ta	—	(0.11)	(<0.01)	(<0.01)
B	—	—	.0040	.0015
Zr	—	(0.03)	.050	.027

[a] Size: Disks 1¼-in. in diam. and ¾-in. thick.

[b] Dashes indicate elements not certified.

[c] Values in parenthesis are *not* certified but are given for information on the composition.

The compositions of the six new standards together with those of the three existing standards are given in Table I. The results are the averages of determinations made by the National Bureau of Standards, Washington, D. C., Allegheny-Ludlum Steel Corporation, Brackenridge, Pa., and Ordnance Corps, Watertown Arsenal, Watertown, Mass. In addition, the Crucible Steel Company of America cooperated in the analysis of the 6 Al - 4 V standards, and Ordnance Corps, Frankford Arsenal, Philadelphia, Pa. and Ledoux and Company, Teaneck, N. J. cooperated on the analysis of the 8-Mn standards.

The samples are in the form of disks (1¼-in. in diam., ¾-in. thick) which may be purchased from the Standard Sample Clerk, National Bureau of Standards, Washington 25, D. C. The fee is $20.00 per sample.

High Temperature Alloys

Four new standard samples of high-temperature alloys have been added to the four previously made available from the National Bureau of Standards for application to both optical emission and x-ray fluorescence methods of analysis. The new standards are for 16-25-6 (Cr-Ni-Mo), Inconel "X", Waspaloy, and Waspaloy Modified.

Also commonly referred to as "super alloys", these alloys are heat-resistant materials having superior strengths at high temperatures and are used largely in the aircraft and missile industrial fields. Because of the complex composition of these materials and the time consuming nature of chemical analysis, spectrochemical and x-ray methods are used to control their quality in production.

In all, some 23 high-temperature alloys are planned for certification. Although material for some standards was air-melted at Cannon-Muskegon, Muskegon, Mich., most have been vacuum-melted and cast at Allvac Metals Co., Monroe, N. C. All ingots were processed to obtain materials of high homogeneity, and this was confirmed by extensive testing at the National Bureau of Standards.

The compositions of the four new standards are given in Table II. The results are the averages of determinations made by the National Bureau of Standards, Washington, D. C., Armco Steel Corp., Research Laboratory, Middletown, Ohio, Cannon-Muskegon, Muskegon, Mich., Carpenter Steel Co., Reading, Pa., Crucible Steel Co. of America, Syracuse, N. Y., General Electric Co., Schenectady, N. Y., The International Nickel Co., Huntington, W. Va., Ladish Co., Cudahy, Wisc., Ledoux and Co., Teaneck, N. J., Union Carbide Metals Co., Niagara Falls, N. Y., and the U. S. Steel Corp., Applied Research Laboratory, Monroeville, Pa.

The samples are in the form of disks (1¼-in. in diam. and ¾-in. thick) which may be purchased from the Standard Sample Clerk, National Bureau of Standards, Washington 25, D. C. The fee is $18.00 per sample.

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Comparison of Ignited Arc Sources

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Abstract

A *Bardócz BIG 210* ignited arc source was compared with a conventional ignited unidirectional arc and a *Multisource* for the analysis of lead alloys and the determination of boron in steel. The sources performed similarly except for the lead alloy analysis where the *Bardócz* source proved superior in repeatability and line-to-background ratio.

Introduction

A *Bardócz BIG 210* ignited arc source was loaned to us by the *Jarrell-Ash Company*. The *Bardócz* source has been very well described and documented in the literature (*1,2,3,4,5,6*). The *BIG 210* source differs from other ignited arc units in that the igniting spark is electronically controlled and the time of ignition can be varied to produce arc current pulses of varying lengths. The ignitor itself also differs from most other sources in that a *Tesla* transformer is used and the resulting igniting spark contributes very little to the vaporization and excitation of the sample.

To evaluate the above characteristics, the *Bardócz BIG 210* source was compared with a *National Spectrographic Sales Corporation Uniarc* for the determination of boron in steel and with the *Uniarc* and an *Applied Research Laboratories Multisource* for the analysis of lead alloys.

Experimental

Operating Characteristics of BIG 210

To facilitate the intercomparison of the arc sources the operating characteristics of the *BIG 210* source were investigated. Table I shows how the duration of the arc discharge varies as the position of the phase switch is changed. The values were obtained by observing a current trace on a *Tektronix* Type 511A oscilloscope. These six arc duration settings in conjunction with the ten arc current switch settings, which vary the resistance in the circuit, yield sixty source conditions. The average current for these sixty combinations was measured by placing a d.c. ammeter in the circuit and using unidirectional operation. The values varied from 0.01 to 5 amp and it was possible to obtain the same average current with various combinations of arc duration and resistance.

Average current rather than rms current values were measured because the average current has more significance with respect to the energy dissipated in the arc gap (*7,8*).

Boron in Steel

Preliminary experiments with the *BIG 210* indicated that the conditions shown in Table II, which are very similar to those recommended by Rozsa and Zeeb (*9*), were the most satisfactory for boron in steel.

For both source conditions the following were used: *Bausch and Lomb Littrow-Echelle* spectrograph (prism dispersion), ASTM C-5 graphite counter electrode, 20 sec exposure with no preburn, SA#1 plate, 20 μ slit, and seven *General Motors* steel standards with a range of 0.0003% to 0.0042% boron.

TABLE I. DURATION OF DISCHARGE

Arc	*Phase Switch Position*					
Duration	*1*	*2*	*3*	*4*	*5*	*6*
Millisec	0.24	0.89	1.94	3.23	4.03	5.49
% of ½ cycle	3	11	23	39	48	66

TABLE II. CONDITIONS FOR BORON IN STEEL

	Uniarc	*BIG 210*
rms current	7 amp[a]	7 amp[b]
average current	2.60 amp[c]	2.90 amp[c] phase switch, 4 current switch, 9
sample polarity	positive	positive

[a] measured with the thermocouple type rf ammeter built into the source
[b] measured with an a.c. ammeter
[c] measured with a d.c. ammeter

Three exposures were made on each standard under each of the two source conditions. Figure 1 shows the analytical curves and indicates that the values obtained with the *BIG 210* give a better fit than those obtained with the *Uniarc*. This is difficult to understand in view of the poorer repeatability of the *BIG 210* as indicated in Table III.

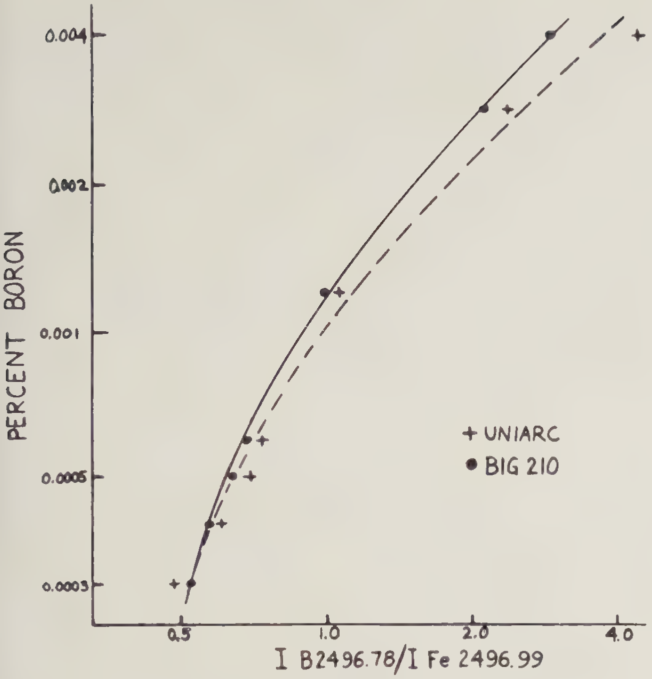

Fig. 1. Analytical Curves for Boron in Steels Using BIG 210 and Uniarc Sources

Lead Alloys

The conditions and equipment for comparing the *BIG 210*, *Uniarc*, and *Multisource* for the determination of antimony and tin in lead alloys are given in Table IV.

Preliminary experimental work indicated that adequate sensitivity for antimony and tin could be obtained with the Phase 2 setting of the *BIG 210* source. Although the same average current could be obtained with Phase 1 and higher settings of the arc current switch, it was found that the sensitivity was too low.

Time-of-wait curves were run for all source conditions and showed that no preburn was necessary.

To determine the repeatability twelve or more determinations were made on a lead alloy sample which previous experience has indicated to be very homogeneous. The results of these determinations are shown in Table V.

A statistical comparison of these data by means of *F* tests at the 95% confidence level shows the *BIG 210* source to be significantly better than either the *Multisource* or *Uniarc* for the determination of tin in lead alloys. Similarly, for the determination of antimony in lead alloys, the lowest current *BIG 210* condition is about the same as the *Multisource*, and both these conditions are better than the others. The variation in apparent concentration, particularly for antimony has been noted in previous work on this alloy. Different source conditions tend to give different results and there is evidence that the shape of the antimony analytical curve changes. This curve change and the fact that the analyses are extrapolated from the range covered by the standards may account for the variation.

The analytical curves for antimony obtained with the *BIG 210 A*, *Uniarc*, and *Multisource* conditions indicated a better line-to-background ratio for the *BIG 210 A* condition. The tin analytical curves indicated that the backgrounds were about equal.

Table III. Coefficient of Variation for Boron in Steel[a]

		BIG 210	*Uniarc*
3 standards	>0.001% B combined	17%	8.8%
3 standards	<0.001% B (excluding 0.0003% B) combined	33%	8.5%

[a] the values were combined by taking the rms of the coefficients of variation.

Table IV. Conditions for Lead Alloy Comparison Using BIG 210, Multisource, and Uniarc

Sources		*Arc Current*	I_{av} [a]
BIG 210 A,	Phase 2,	3	0.11
BIG 210 B,	Phase 2,	4	0.14
BIG 210 C	Phase 2,	5	0.20
Multisource,	2μf-730μh-100		0.10
Uniarc,	Arc Power 1		0.50

Analytical Lines	*Excitation Potential, e.v.*	*Concentration Range*
Pb I 3220.54	6.47	Internal Std.
Sb I 3267.50	5.82	0 - 20%
Sn I 2913.54	6.38	0 - 10%

Spectrograph: *ARL, Industrial Research Quantometer*

Electrodes: Sample, upper electrode, polarity negative, counter electrode ASTM C-5, 3 mm gap

Exposure: 0 sec preburn, approximately 20 sec exposure, (exposure for constant lead intensity)

Analytical Curves: Determined by *Morris P. Kirk* Linotype Standards 524, 525, 526

[a] Amp

An interesting feature of the data in Table V is the increase in repeatability as the average current decreases for the three *BIG 210* conditions. Attempts to operate the *Uniarc* at lower average currents by modifying the circuit were unsuccessful and the condition given in Table IV was the lowest current obtainable for stable operation. Data were also collected for the *Multisource* operated at 700 volts instead of the normal 940 volts and no improvement in repeatability was obtained.

It was apparent from the physical appearance of burns that the initiating spark for both the *Multisource* and *Uniarc* conditions contributed much more to the excitation and spectral background than the *BIG 210* initiator. Appreciable lead line intensity was observed when only the initiators on the *Multisource* or *Uniarc* were operated while none was observed for the *BIG 210* initiator.

Low Alloy Steel

The low current *BIG 210* conditions that proved successful with lead alloys were found to give insufficient

Table V. Analysis of Lead Alloys-Repeatability Using BIG 210, Multisource, and Uniarc

Antimony					
Source	$I_{av.}$ [a]	*% Sb*	*Standard Deviation*	*Coefficient of Variation*	*Number of Values*
BIG 210 A	0.11	9.56	0.172	1.80	12
BIG 210 B	0.14	9.39	0.228	2.43	29
BIG 210 C	0.20	9.45	0.274	2.89	12
Multisource	0.10[b]	10.10	0.163	1.61	19
Uniarc	0.50[b]	8.58	0.302	3.52	31
Tin					
Source	$I_{av.}$ [a]	*% Sn*	*Standard Deviation*	*Coefficient of Variation*	*Number of Values*
BIG 210 A	0.11	5.88	0.042	0.72	12
BIG 210 B	0.14	5.58	0.061	1.09	29
BIG 210 C	0.20	5.88	0.068	1.16	12
Multisource	0.10[b]	5.70	0.161	2.82	15
Uniarc	0.50[b]	5.80	0.202	3.48	31

[a] Amp

[b] Current of d.c. component does not include initiator

intensity for convenient direct-reader analysis of low alloy steel. At higher currents, the *BIG 210* yielded repeatabilities of 5% to 10% coefficient of variation and performed about the same as other high voltage or ignited arcs.

Summary

The characteristics of the *Bardócz BIG 210* source are essentially those of an ignited a.c. or uni-directional arc. The use of a weak *Tesla* discharge in the ignitor results in improved line-to-background ratio at low currents since the igniting spark contributes very little to the sample excitation. Very low average currents are obtainable and may be useful for the analysis of low boiling point materials such as lead alloys.

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Spectrographic Analysis of Hafnium By a Point-to-Plane Technique†

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Abstract

A method has been developed for the analysis of hafnium metal for aluminum, copper, iron, titanium, and tungsten in the ppm range and zirconium in the 1.0-4.0% range. Solid machined pieces 1 x 1 in. or larger are used. Spectra are excited with a low voltage ignited ac arc with low inductance and capacitance. Hafnium serves as the internal standard. The method offers an increase in speed and improved precision over the carrier distillation technique which has been commonly used.

Introduction

Hafnium metal is used in the manufacture of control rods for pressurized water nuclear reactors because of its high neutron capture cross section, mechanical properties, and good corrosion resistance. These desirable properties are altered by the presence of impurities; zirconium lowers the effective neutron capture cross section, and other impurity elements may change its mechanical properties and corrosion resistance. Maximum allowable levels of impurities in hafnium to be used in a naval nuclear reactor *(1)* are shown in Table I. In order to meet the analytical requirements of this specification, a rapid and precise method of analysis capable of detecting at least half of the maximum allowable concentration for each impurity was desirable. Most spectrochemical methods previously used were variations of oxide powder approaches utilizing either carrier distillation or buffer *(2,3)* and were insufficiently precise. The chemical methods used were lengthy. As all samples were available in dense metallic form a point-to-plane technique was preferable if it could meet the other requirements.

Procedure

Standards and Samples

Standards for hafnium were not available commercially or from the Atomic Energy Commission. In order to obtain standards, the results of all hafnium metal analyses previously performed in our laboratories were examined. From these data, specific ingots were selected for further evaluations. Tensile pieces and end croppings from these ingots were then assembled and chemically analyzed. When repeated chemical analysis indicated good homogeneity the pieces were accepted as standard. This homogeneity was confirmed spectrographically for most standards. Solid pieces of hafnium previously machined for hardness and density test provided the necessary samples for development of a point-to-plane technique. The samples were flat pieces with a 32 micro-inch finish and were cleaned with a 5% solution of HCl in alcohol before use.

Operating Conditions

The conditions and apparatus used are given in Table II. During the investigation of the optimum setting, a hemispherical type of electrode was tried as the lower electrode, but it gave higher background than the cone electrode. The sample was the upper electrode. The source conditions previously employed in Zircaloy analysis for the determination of aluminum and titanium when applied to the hafnium analysis permitted detection of all the elements sought except tungsten. To vaporize and excite tungsten,

TABLE I. QUALITY CONTROL SPECIFICATIONS FOR HAFNIUM *(1)*[a]

Element	*Concentration, ppm*
Hafnium	95.3[b]
Zirconium	4.5[b]
Aluminum	100
Copper	100
Hydrogen	25
Iron	500
Nitrogen	100
Titanium	100
Tungsten	300
Uranium	20

[a] All are maximum values except for hafnium.
[b] Given in %.

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†Presented at the Tenth Annual Symposium on Spectroscopy, Chicago Section, Society for Applied Spectroscopy, Chicago, Ill., June 4, 1959.

*Present address: Texon, Inc., So. Hadley Falls, Mass.

Table II. Apparatus and Operating Conditions

Spectrograph	3.4 M Ebert Jarrell-Ash with grating, 15,000 lines/in.
Slit width, μ	20
Electrode	Graphite, 120° cone
Diam., in.	¼
Excitation Unit	Jarrell-Ash Custom Varisource Ignited ac arc circuit
Analytical gap, mm	2
Spark, primary, v	200
resistance, ohm	23
Spark, secondary, r.f. amp	7.5
Inductance	Residual
Capacitance, μf	0.0025
Resistance	Residual
Breaks/half cycle	14
Arc current, r.f. amp	3.8 ± 0.1
Preburn, sec	2
Exposure, sec	10

Table III. Analytical Lines and Concentration Ranges of Impurity Estimation

Element	*Wavelength, A*	*Background Correction*	*Present Calibration Range*	*% of Light Transmitted by Sector*
Hf	2951.9	No	Matrix	25
Zr	3270.6	No	1.0-4.0%	25
Al	3082.2	Yes	20-150 ppm	25
Cu	3273.9	No	5-150 ppm	25[c]
Fe	2994.4	Yes	20-500 ppm	100
Ti	3349.4	Yes	10-100 ppm	25
W (1)	2944.4	Yes	20-300 ppm[a]	100
W (2)	2896.4	Yes	30-500 ppm[b]	100

[a] Fe interference above 500 ppm

[b] No Fe interference until at least 2000 ppm

[c] Additional filtering may be desirable.

it was necessary to increase the spark power using the parameters given in Table II. Samples were always allowed to return to room temperature before a second exposure. A minimum limit of 1″ x 1″ x ⅛″ was set for the sample size.

Line Selection and Working Curves

Hafnium containing a small percentage of zirconium gave a very complex spectrum as shown in Figure 1. As an aid to line selection a piece of hafnium was scribed with rods of pure aluminum, copper, iron, and titanium. This hafnium was then burned over each scribed area and the spectra emitted by those areas were compared to the spectrum of an unscribed portion of the sample. The Hartman diaphragm method of matching spectra was employed for tungsten and zirconium. The prominent lines of each element were studied for possible interference by directly matching the spectra. A subsequent cross check was made using the MIT Wavelength Tables *(4)*. Some discrepancies seem to exist in the identification of certain hafnium and zirconium lines listed in the tables and special care was exercised in selecting lines for those elements.

The wavelengths and range of calibration of the analytical lines as well as % transmission of the rotating filter are shown for each line in Table III.

The working curves have been drawn from data obtained with selected standards. Some elements, such as iron, presented calibration difficulties because of their nonhomo-

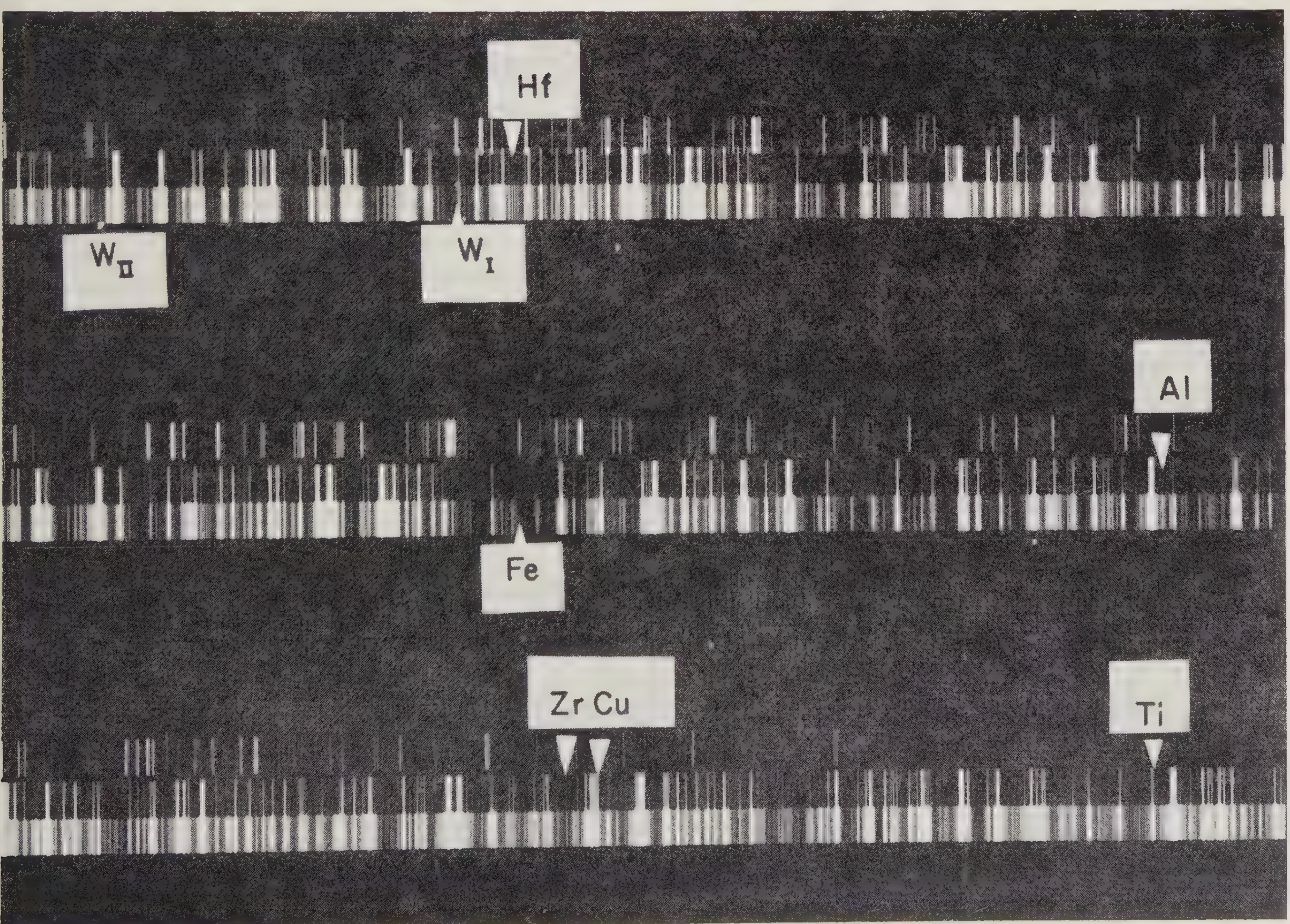

Fig. 1. Hafnium Spectrum with Analytical Lines Marked

geneous dispersion in hafnium. Copper, iron, aluminum, and tungsten have parallel curves. Zirconium has a curve close to a 45° theoretical slope. In the case of titanium, the inclination of the curve is much steeper.

Moving Plate Study

A moving plate study was made in order to determine the vaporization-excitation characteristics of the various elements. Successive ten-sec exposures from a single burning were recorded. The plotted curve (Figure 2) shows an increase in transmission reading with time for all impurities. Hafnium and zirconium curves are almost identical. Aluminum and titanium curves, in general, parallel the hafnium curve. Tungsten and iron curves, although having a slope similar to the hafnium curve, do not parallel it closely. The greatest variation from the internal standard was observed with the copper curve. Considering that the transmissions for the copper line are very low, on the order of 4 to 7%, it is probable that this variation is related to the measurement of the very intense lines. No other copper lines were found satisfactory with the setup used, but additional filtration could be easily added if necessary to improve precision. The relative precision for each element can be predicted from this plot. Impurity determinations will have greater precision when the vaporization-excitation curve for the impurity closely parallels the internal standard curve. Statistical studies confirmed these predictions.

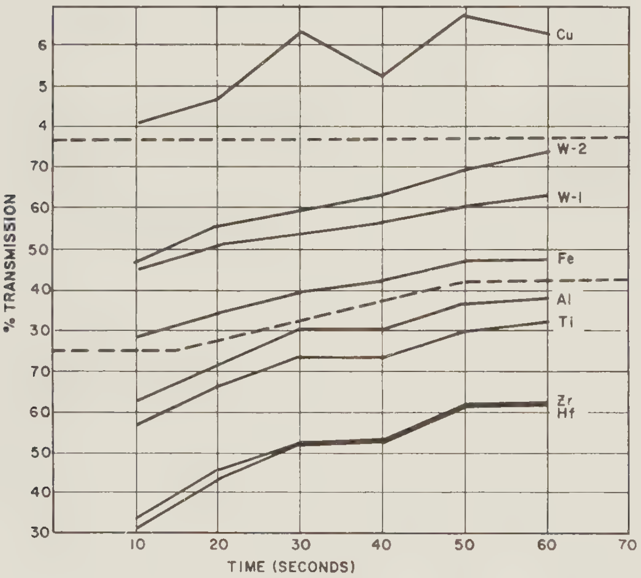

FIG. 2. MOVING PLATE STUDY

Precision and Accuracy

The hafnium sample used for statistical studies had a weld on the lower section. This welded part was cut off and chips milled from the fresh surface for wet chemical analysis. The two faces of the other section were machined to a flat surface and spectrographically analyzed. To evaluate the accuracy and precision of the method, fourteen burns were obtained on the machined surface of the sample in a single day. This was repeated four times. A minimum of a week elapsed between each set of analyses with no recalibration of the working curves during the entire period.

The test piece, based on four sets of analyses, showed areas of varied impurity content. Areas of segregation were identical for all elements and similar on both sides of the piece. The definite nonhomogeneity of the sample was statistically restrictive for the precision study; therefore, areas of low impurity levels were excluded from the statistical analysis.

TABLE IV. PRECISION STUDIES

	Al	*Cu*	*Fe*	*Ti*	*W*	*Zr*
Ave. Std. Dev. (Single Burn)						
(for one day)	7.9	4.6	18.4	1.2	14.0	.11
(for one month)	10.4	4.4	18.6	1.1	16.8	.11
Analysis of Test Piece (ppm)	113	32	150	20	138	2.2[a]

[a] Given in %.

The standard deviations for each element in each set of eight exposures shown in Table IV were calculated according to standard formulas. These data represent the average precision to be expected for a single exposure per analysis. Precision can be increased, if desired, by making more than one exposure, since for n exposures, the standard deviation is decreased by the factor $1/\sqrt{n}$. The standard deviation calculated for each element with all values collected over a period of a month is also given. Since no recalibration of the curves was made, the precision over a period of a month is a good indication of the stability of the working curves.

TABLE V. COMPARATIVE ANALYTICAL RESULTS. TEST PIECE

Method	*Al* *ppm*	*Cu* *ppm*	*Fe* *ppm*	*Ti* *ppm*	*W* *ppm*	*Zr* *%*
Spectrographic	118	30	156	15	145	2.2
Chemical	113	32	150	20	138	2.2[a]

[a] X-ray Fluorescence

Table V shows the accuracy of the method as evaluated from the test piece. As previously mentioned, the sample for chemical analysis was taken from the piece bearing the weld and the number shown for the spectrographic value is the average of all the values obtained for the bottom two rows of analyses from both sides of the sample. Zirconium in hafnium was determined independently by an absolute method based on x-ray emission spectroscopy.

Table VI shows a comparison of values obtained by the point-to-plane technique and values reported by three other laboratories. The samples analyzed were hafnium buttons melted from sponge material. Their impurity level was quite high and some values were determined by extrapolating the working curves. The results from the point-to-plane technique generally agreed with Laboratories B and C for iron, titanium, and zirconium and agreed with Laboratory A for aluminum. No explanation for the disagreement with Laboratory B on the aluminum values is available. It is interesting to note that all iron values re-

TABLE VI. COMPARISON DATA ON HAFNIUM SPONGE SAMPLES[a]

			Laboratory		
Element	*Sample*	*Point-to-Plane Method*	*A*	*B*	*C*
Al	A	53	47	70	Not reported
	B	115	103	101	
	C	21	25	49	
Fe	A	475	131	480	490
	B	2800	556	2250	>2000
	C	240	76	300	315
Ti	A & B	Considerably above calibration range			
	C	60	10	63	85
Zr	A	2.8	2.2	2.8	2.9
	B	3.7	2.8	3.5	3.7
	C	2.6	2.2	2.6	2.8

[a] All values reported as ppm except the Zr results which are in %.

ported by Laboratory A are about one-fourth the values reported by the other laboratories. The zirconium values reported by Laboratory A appear to be biased low. It is expected that even better agreement between laboratories will be reached when ingots of low impurity content can be used for comparison.

Conclusion

The point-to-plane technique (incorporating an ignited a.c. arc), when used in the determination of hafnium impurities, is superior in precision, accuracy, and requires 75% less time than other methods used in our laboratory.

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A Spark Spectrographic Procedure For the Determination of Boron in Sheet Steel

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Abstract

Sheet metal is directly analyzed for boron by means of spark excitation. Source inductance of 200 to 300 μh, together with rotation of the specimen during excitation, provides detectability an order of magnitude better than conventional spark excitation of steel. Sheet material of 0.050 in. thickness and containing a nominal 0.004% boron is analyzed with a coefficient of variation of 3.2%.

Introduction

Commercial applications of boron-treated steels are critically dependent on boron content and distribution within the alloy. Control of the very low effective quantities of boron has introduced serious problems in both metallurgical technology and analytical techniques. The tendency of boron to diffuse readily at high temperatures and combine at the surface with oxygen and nitrogen, has troubled the metallurgist in the preparation of reliable compositions. Likewise, these same tendencies are detrimental to precise spectrographic determination of boron when the steel is subjected to high temperature arc excitation. The sensitivity of boron line emission to specimen temperature has been repeatedly emphasized in published spectrochemical methods for the determination of boron in steel. Successful analytical procedures have included a variety of precautionary measures to insure acceptable reproducibility of boron emission from exposure to exposure.

Corliss and Scribner *(1)* noted the necessity of precise control of self-electrode diam., and the projected length of self-electrodes in the mounting of small rod-type samples. Runge, *et al (2)* have emphasized the rapid depletion of boron during arc excitation and the desirability of superimposing short exposures obtained from specimens not previously arced. The status of boron determination in steel using arc discharges on massive samples, rods, and drillings has been reviewed by Steinberg *(3)*. Arc excitation of metal chip compacts has been reported *(3)*, and recently Paterson *(4)* has devised a fluoride evolution procedure employing arc excitation, which is applicable to materials in chip form.

The above methods have been useful for analyzing boron steels produced as ingot, plate, and rod. However, these methods have not been found appropriate for the direct determination of boron in sheet stock. For example, an ac arc method which provides a coefficient of variation of 5% on rods and massive amples may show a 15% variation on 0.050 in. sheet. In order to determine boron accurately in sheet material it was decided to investigate means of keeping the relatively thin sample cool during excitation. This program involved exploration of the characteristics of spark sources with respect to detectability and reproducibility of boron determinations in sheet material.

Experimental

Since the 2496. 78 A boron line is the most practicable line available, and since this line is classified as having equal intensity with either arc or spark excitation *(5)*, it first appeared appropriate to determine at what concentration level boron would be detectable using a convenional spark source designed for steel analysis. The faint detection of boron in the presence of heavy background occurred at the concentration of 0.02%. The problem then appeared to be the usual one of enhancing line intensity in reference to background.

Line Enhancement

Boron line intensity has been previously enhanced *(2)* by selection of an exposure period to coincide with maximum line emission occurring during the first few sec of excitation. Improved boron detectability has also been obtained by superimposing several such exposures from a series of individual samples *(2)*. In order to exploit these enhancement factors, line intensity versus time (time-of-wait) data were obtained using spark excitation on a sample of high boron content together with a fast photographic emulsion. Also, new sample surface is introduced during these exposures by rotating the flat sheet specimen at a speed which provides new sample at an optimum rate as determined by the time-of-wait data. This latter principle of line enhancement has been independently demonstrated by Eckhard and Koch *(6)*.

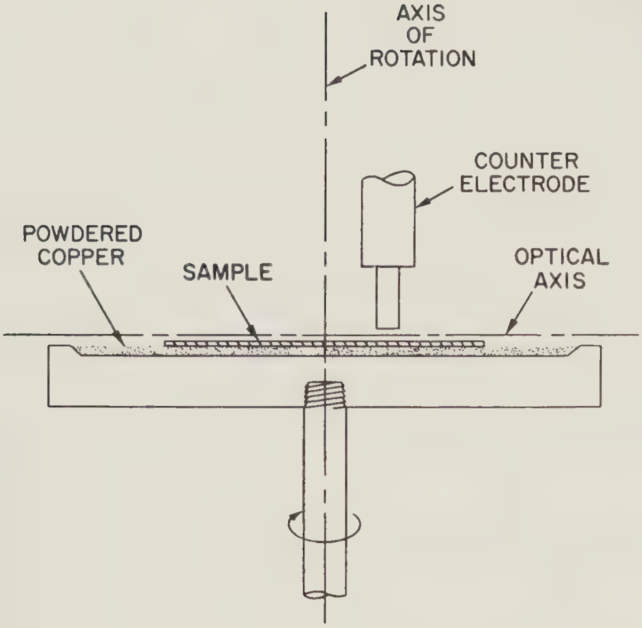

FIG. 1. ROTATING SPECIMEN SUPPORT FOR THE ANALYSIS OF SHEET MATERIALS

With spark as well as with arc excitation it is necessary to provide adequate thermal and electrical conductivity between the sample and the rotating supporting platform. Thin sheet samples will become overheated and produce erratic results unless the entire flat surface is in contact with a relatively massive metal base. A sample support consisting of a heavy circular copper tray was devised as shown in Figure 1. It is constructed of brass with the thick platform acting as a heat sink. The recessed top surface will hold a 0.16 cm deep layer of powdered copper on which the sample is pressed to provide uniform thermal and electrical contact with the lower sample surface. Since sheet stock is seldom perfectly flat, it is imperative that some means of assuring uniform physical contact be provided. The powdered metal contact described has been found more satisfactory with the rotating support than mechanical clamping methods.

Spark discharge time-of-wait data for stationary and moving samples are plotted in Figure 2. Line transmittance versus time, in the case of the stationary sample, indicates highest line intensities for both boron and an homologous iron line during the first ten-sec interval. Intensity then diminishes rapidly during successive intervals. Rotation of the sample at the rate of 1 rpm, however, allowing the spark to traverse a circle of 1.6 cm diam., provides relatively high boron line intensities over almost the entire period of revolution. Thus the integrated intensities for a one-min exposure are considerably improved by employing the rotating sample.

Background Suppression

Generally recommended spark-sources *(7)* for the excitation of steel operate with little or no added inductance. The low inductance aids in analytical precision but contributes background detrimental to trace element determinations. To investigate the effect of inductance on the boron line relative to background, transmittance measurements were made on spectra produced with inductance values ranging from residual to 1250 μh. Figure 3 depicts changes in photographic density values with changes in source inductance. Microphotometer measurements were made at 2496.8 A to obtain density values for line plus background for each inductance setting. Background readings were taken immediately adjacent to the boron line. From these microphotometer values the background-corrected boron line densities were obtained according to the method of Nachtreib *(8)*. Total boron plus background density decreases almost linearly with added inductance. Background intensity alone diminishes somewhat asymptotically as expected, when inductance is increased. Boron line density alone is favored when inductance values lie in the neighborhood of 200-300 μh. Favorable line-to-background ratio is achieved by selection of an inductance value of about 300 μh. Precision considerations however lead one to select the lowest inductance compatible with the detectability required. Subsequent experiments therefore involve an inductance of approximately 200 μh.

Results

The range and precision of analysis of boron steel sheet of 0.05 in. thickness are determined by means of a spark procedure incorporating the sensitivity enhancement techniques described above. Standard samples consisting of cold rolled specimens of chemically and spectrochemically analyzed steel† containing boron in a concentration range from 0.003 to 0.020% are believed to be reliable to ±0.0003% boron. The sample surface is ground clean prior to sparking, and sample areas once sparked are not considered reliable for subsequent use as standards.

Measurement of the lines B 2496.78 A and Fe 2487.07 A provides an essentially linear analytical curve for the range 0.003 to 0.02% boron when a single 55 sec exposure is used. The concentration index for this analytical line pair is 0.006% boron. Detectability is about an order of magnitude better than conventional spark procedures for

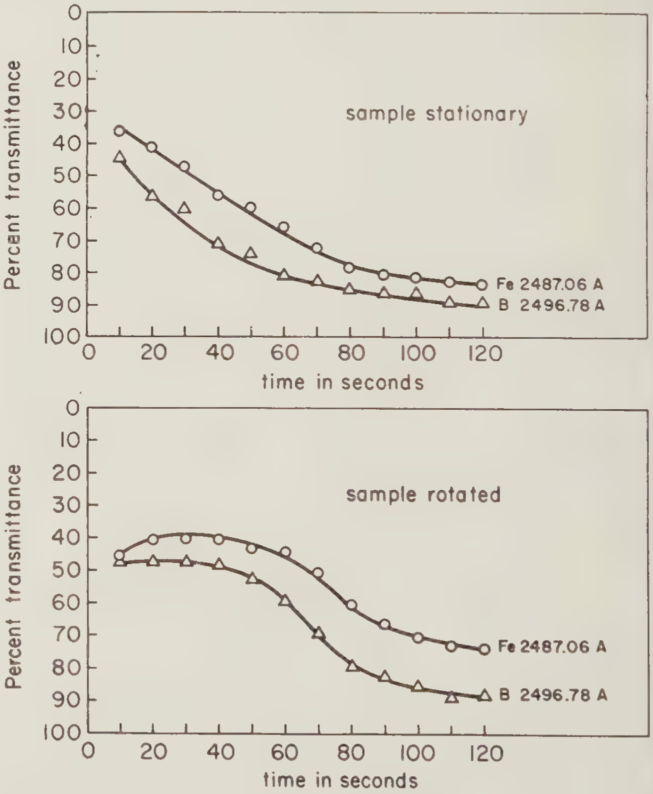

FIG. 2. SPARK EXCITATION CHARACTERISTICS OF FE AND B LINES IN STEEL

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†Supplied through the courtesy of Mr. James E. Paterson, Graham Research Laboratories, Jones and Laughlin Steel Corporation, Pittsburgh, Pa.

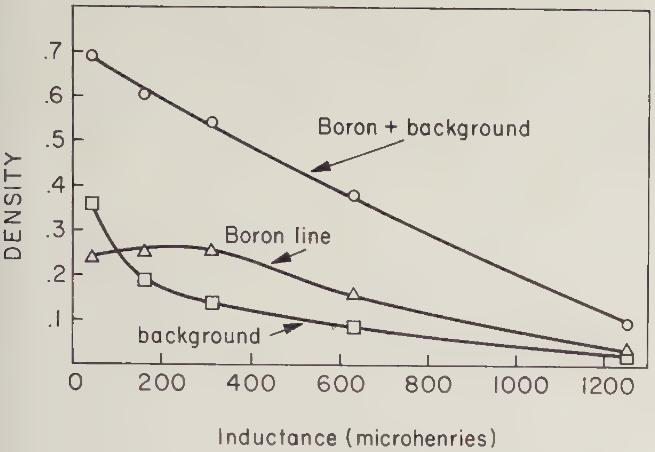

Fig. 3. Effect of Inductance on Photographic Densities of Boron Steel Spectrum

steel analysis. Although no sheet standard below 0.003% was available, there is evidence from more massive standards that 0.001% boron would be detectable in sheet by means of spark excitation. The operating conditions and apparatus used are given in Table I.

Table I. Apparatus and Spectrographic Operating Conditions

Electrodes: Sample	Steel plate
Counter	5/16-in. diam. graphite rod, machined to 1/8-in. diam. for lower 3/8-in. of length
Analytical gap, mm	2
Excitation unit	Jarrell-Ash Varisource, high-voltage spark
Primary resistance, ohm	6
Capacitance, μfd	0.015
Inductance, μh	200
Resistance, ohm	1
Current, r.f. amp	8.5
Discharges per half-cycle	3
Spectrograph	Jarrell-Ash 3.4-meter Ebert, 15,000 lines per in. grating, second order
Wavelength range, A	To include 2480 to 2500
Slit width, μ	20
Sector	None
Filter	None
Photographic emulsion	Eastman SA-1
Developer	Kodak D-19, 19° C, 3 min
Plate calibration	Separate stepped-exposures of iron arc, providing lines of known relative intensity, according to the method of Dieke.

Precision of boron determinations in sheet steel by this modified spark procedure appears superior to arc procedures as applied directly to sheet stock and is comparable to arc procedures applied to rods and massive samples. Table II presents repeatability data using the high-inductance spark with rotating sample. Ten separate samples cut from the same sheet provide an average concentration value of 0.00426% boron. Maximum deviation from the mean is 0.00026% boron; cofficient of variation is 3.17%.

Table II. Repeatability of Boron Determinations in Sheet Steel Using High-Inductance Spark Excitation and Rotating Sample[a]

No.	*% T* 2487.07 Fe	2496.78 B	*Log I/Io*	*% Boron*	*Deviation from Mean*
1	23.1	37.9	$\bar{1}.83$	.0043	.00004
2	20.8	32.9	$\bar{1}.85$	.0044	.00014
3	20.2	31.2	$\bar{1}.84$	.0044	.00014
4	20.3	33.7	$\bar{1}.82$	.0042	.00006
5	17.6	30.9	$\bar{1}.80$	.0040	.00026
6	18.5	29.4	$\bar{1}.84$	.0044	.00014
7	20.2	34.2	$\bar{1}.83$	.0043	.00004
8	19.0	31.3	$\bar{1}.82$	.0042	.00006
9	17.8	21.0	$\bar{1}.81$	.0041	.00016
10	19.8	32.1	1.83	.0043	.00004
			av. =	.00426	

[a] $v = (100/c)\sqrt{\Sigma d^2/n-1} = 3.17\%$

Conclusions

Direct spark excitation of sheet steel is capable of providing suitable detectability and precision for boron determinations in the commercially important concentration region of 0.01% boron. Detectability is superior to conventional spark excitation of steels. Precision is superior to direct arc excitation of sheet stock.

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Submitted December 29, 1959

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Sensitometric Properties of a Polaroid Emulsion as Applied to Spectroscopic Analysis

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Abstract

Polaroid-Land Type 46-L Projection Film is investigated as a medium for recording optical spectra for the purpose of qualitative and quantitative spectrochemical analysis. The film's high spectral sensitivity extends from 3000 to 6000 A. In the analytically important 3000-4000 A region, emulsion contrast is found to be adequate and reasonably constant; gamma averages to about 2.3 and is reproducible to within ±0.1 from frame to frame. Speed is sufficient for nearly all spectrochemical purposes. Resolution of at least 30 lines/mm is obtainable. Analytical precision resulting in a coefficient of variation of less than ±5% indicates that Polaroid films are likely to find some utility in quantitative as well as qualitative analysis.

Spectrographic analytical procedures, both qualitative and quantitative, have since their inception required photographic techniques involving elaborate facilities and time-consuming processing. Minimum facilities for obtaining the simplest type of spectrum have included a darkroom, a series of chemical processing tanks and solutions, rinsing and drying equipment. Minimum processing time is normally from 10 to 20 min providing the system is pre-established and familiar, with safelights pre-selected and solutions pre-prepared. These times may be at least doubled in situations where spectra are only occasionally processed, or where untrained personnel are involved.

With the advent of "one-minute" daylight processed films such as the Polaroid type, it is conceivable that some classes of spectrographic analyses, namely qualitative and semi-quantitative, can be accomplished with a great savings in facilities and time. With these possibilities in mind, some experiments are made to assess the characteristics of a typical Polaroid emulsion in reference to requirements for spectrographic analysis.

The emulsion investigated is the type 46-L Polaroid-Land Projection Film which is a roll film resulting in a direct positive transparency of 2¾" x 3½" size. Other similar Polaroid emulsions will provide either negative transparency spectra on film or direct positive spectra on paper. The choice of the positive transparency for this investigation is premised on the immediate availability of a suitable camera back for development of the roll film positives and a conventional micro-densitometer for the photometry of transparencies.

The general properties of spectral sensitivity, contrast, speed, granularity, and resolution are investigated. Throughout the experiments the manufacturer's recommended processing procedure is used. Spectra are produced using a Jaco 3.4 Meter Ebert Spectrograph employing first order (5A/mm) dispersion. A 5.0 amp dc arc across pure iron electrodes provides the source of illumination. For sensitivity and contrast measurements a stepped sector disc is used during a 50 sec exposure for intensity control. Figure 1 shows the Jaco spectrograph plate holder modified for the accommodation of Polaroid type roll films.

Spectral Sensitivity

Qualitative analysis, in particular, is greatly dependent on the wavelength range to which the emulsion is sensitive. Polaroid emulsions, including type 46-L, are reported to have adequate spectral sensitivity in the visible region between 4000 and 6300 A *(1)*. Particularly important to spectrography, however, is the near ultraviolet region below 4000 A, containing many sensitive lines and providing superior dispersion when prism instruments are used.

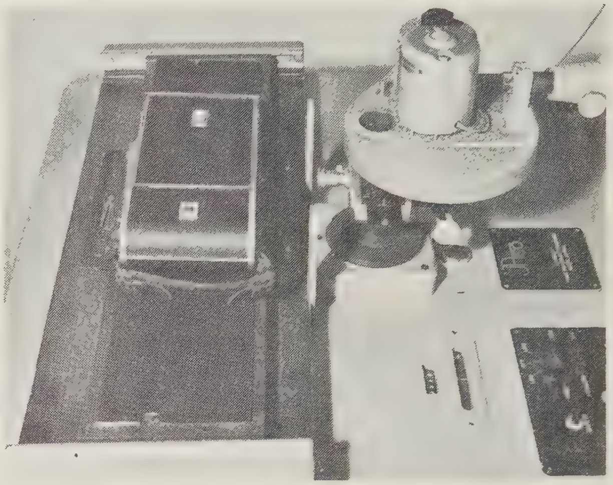

FIG. 1. SPECTROGRAPH EQUIPPED WITH POLAROID-LAND CAMERA BACK

To determine relative sensitivity versus wavelength in the near ultraviolet, a series of equivalent iron arc exposures covering the range from 2500 A to 4000 A is made using a logarithmic step sector having a sector step ratio of 1.58. Iron lines rated with an M.I.T. arc intensity of 500 *(2)* are selected throughout the wavelength range for sensitivity measurements. For each wavelength measured, the relative exposure value at which the line density equalled 0.8 is recorded. These relative exposure values are plotted in Figure 2 as a function of wavelength. For the region 3000-4000 A, the sensitivity is reasonably high and reasonably uniform. Below 3000 A, however, there is evidence that sensitivity may be falling rapidly since an iron line near 2700 A of 500 intensity rating, is not discernable under these exposure conditions. Some of the reduction in apparent emulsion sensitivity may be due to loss in grating speed, since the lower wavelengths are farther from the center of blaze. The combined data, thus far, would indicate that the Polaroid Type 46-L has a useful spectral sensitivity range of at least 3000 A extending from below 3000 A in the near ultraviolet to above 6000 A in the visible red.

Contrast Reproducibility

Following the manufacturer's recommended procedure for film development, a series of sectored exposures of a dc iron arc is obtained to determine the characteristic response curve of the emulsion. Stepped densities of several iron lines in the neighborhood of 3100 A are plotted as a function of the logarithm of the exposure. Since the film photometered is a positive, the toe and shoulder of the curve are inverted in comparison with typically plotted Hurter-Driffield *(3)* curves obtained from negatives. Microphotometer zero and 100% transmittance settings are established by means of background and a very bright line,

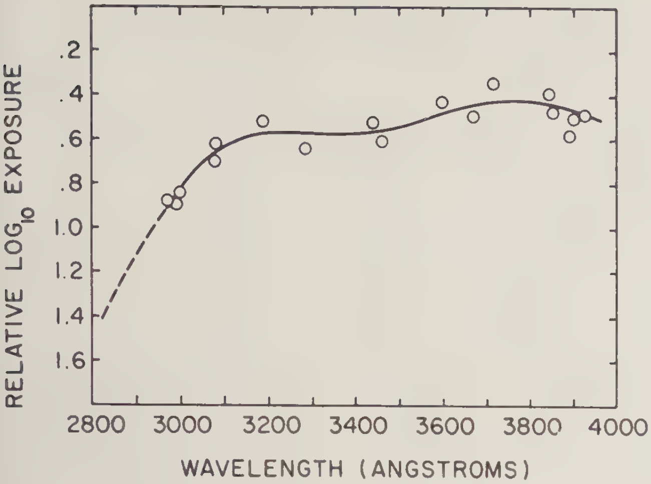

Fig. 2. Relative Exposures Required to Produce a Line Density of 0.8 for a Series of Fe Lines of 500 (M.I.T) Arc Intensity

respectively. From these measurements a composite characteristic curve is drawn which provides the contrast value for the given wavelength. The characteristic curve obtained for the type 46-L emulsion in the vicinity of 3100 A is shown in Figure 3. The straight portion has a slope (gamma) of 2.4, and is essentially linear from density 0.6 to 1.6. The illustrated contrast value and latitude are typical of many measurements subsequently obtained on the 46-L emulsion.

Reproducibility of contrast is determined by recording a sectored exposure of a 50 sec iron arc on each frame of a single roll of film. Each frame is processed separately, according to the manufacturer's recommended procedure. The density of the 3083.74 A iron line is measured for each exposure step and the slope of the straight portion of the characteristic curve determined for each frame. The value of gamma averaged 2.5 for the several frames, with deviations averaging within 0.1 of the mean. Thus, one would expect quantitative spectrochemical applications to be feasible providing there is strict adherence to recommended processing procedure and providing quantitative comparisons involve a single emulsion batch. Reductions in contrast as great as 0.5 are encountered, however, when out-dated film is used, or when hardener solution becomes depleted. Density readings need to be made within a few hr after developing the film, since readings taken a day or so later are not always identical to the earlier values.

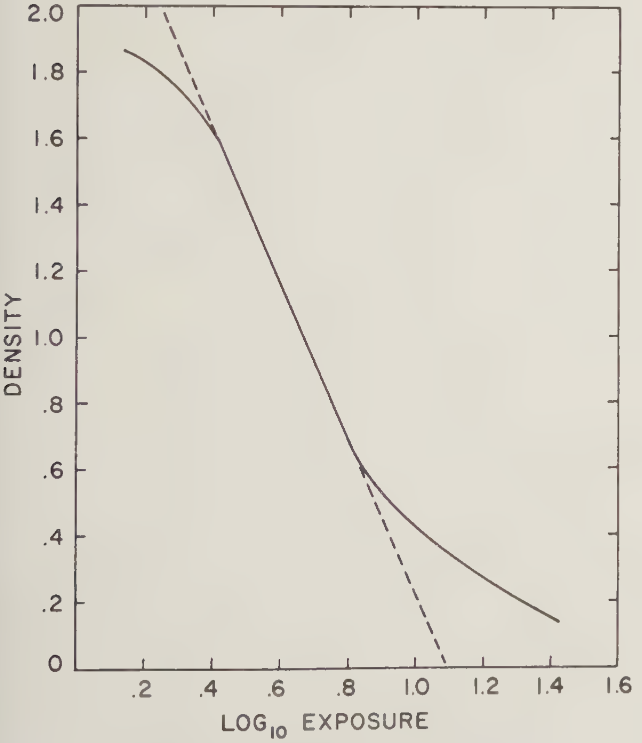

Fig. 3. Emulsion Response Curve for Polaroid Type 46-L Film in the Vicinity of 3100 A

Contrast as a Function of Wavelength

Quantitative analysis, particularly in the case of nonferrous alloy analysis involving line pairs far apart in wavelength, requires that contrast be fairly uniform throughout the range photographed. Again, using the stepped sector, contrast values are obtained at specific wavelengths at intervals of 100 A or less, throughout the near ultraviolet region. Iron lines of sufficient intensity to provide a series of stepped line densities well into the straight portion of the characteristic curve are used to establish slope (gamma) at that particular wavelength. The gamma value obtained for each wavelength measured is plotted against wavelength in Figure 4. These measurements indicate that the contrast of the 46-L emulsion may vary between 2.0 and 2.6 in the 3000-4000 A range.

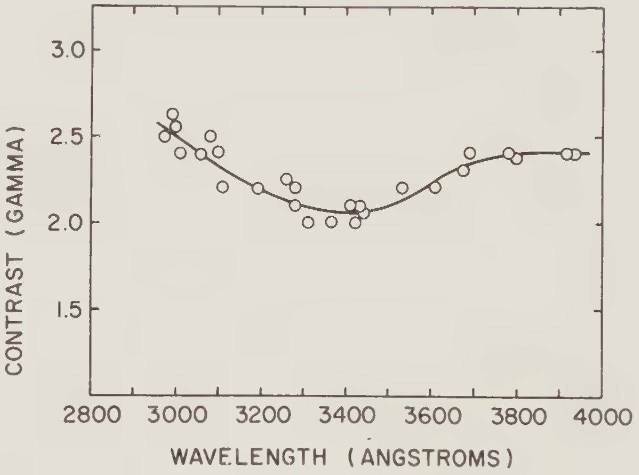

Fig. 4. Contrast as a Function of Wavelength in the Near Ultraviolet Region for Polaroid Type 46-L Film

Speed, Granularity, and Resolving Power

The Polaroid Projection Film, type 46-L, may be qualitatively classified as a relatively high speed (ASA 1000), low inertia emulsion. Exposure periods can be less than one min for most analytical problems.

Grain size viewed at high magnification is found to be adequately fine. Although there is a tendency toward longer range granular structure in the positive transparencies studied, this tendency is not detectable in the corresponding negatives from which the transparencies are transferred.

Resolution is determined by photographing in white light a National Bureau of Standards Resolution Test Chart *(4)*. The camera is equipped with an f/4.7 achromatic objective of 135 mm focal length to assure that the lens does not degrade film resolution *(5)*. The number of

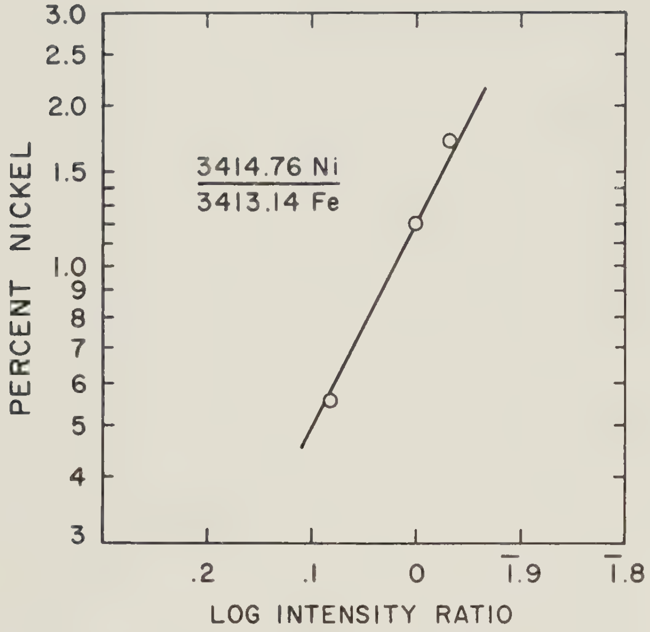

FIG. 5. ANALYTICAL CURVE FOR NI IN STEEL USING THE POLAROID EMULSION

lines/mm visibly separable under these test conditions is 30, or better. The resolving power of the Polaroid Type 46-L is therefore adequate in relation to the conventional requirements of spectrographic analysis.

Analytical Precision

The degree of usefulness of the Type 46-L emulsion for quantitative analysis is determined by means of a series of steel standards together with a calibration curve based on nickel content. Spark excitation is applied to National Bureau of Standards rod specimens containing nickel in the range of 0.5 to 1.7%. The intensities of the nickel line at 3414.7A and an iron reference line at 3413.1A are measured using a microphotometer in order to plot the logarithm of the concentration against the logarithm of the intensity ratios of these two lines. Figure 5 shows the analytical calibration curve obtained. A desirable linear relationship is obtainable over approximately one order of magnitude change in concentration.

Using this same calibration curve, a steel sample is sparked twenty times, and the spectra recorded on two photographic frames of ten spectra each. The resulting nickel concentration values, as read from the calibration curve, range from 1.10 to 1.25% with an average value of 1.17% (Table I). The standard deviation is 0.05% nickel or about 4.5% of the amount of nickel present.

The precision characteristics of the 46-L emulsion, as shown in these experiments, would appear to be in a category similar to the precision of arc sources commonly used in spectrographic analysis. Rapid process films such as the Polaroid Type 46-L, therefore, have definite usefulness in quantitative as well as qualitative spectrography.

Conclusions

The sensitometric properties of the Polaroid-Land Projection Film, Type 46-L, indicate that it should be useful for both qualitative and quantitative spectrochemical analysis in the visible and near-ultraviolet regions of the optical spectrum.

TABLE I. PRECISION OF NICKEL DETERMINATIONS IN STEEL USING POLAROID PROJECTION FILM TYPE 46-L[a]

Frame No.	*Spectrum No.*	*% Nickel*	*Deviation From Mean*
1	1	1.10	0.07
1	2	1.20	0.03
1	3	1.15	0.02
1	4	1.15	0.02
1	5	1.10	0.07
1	6	1.10	0.07
1	7	1.10	0.07
1	8	1.10	0.07
1	9	1.20	0.03
1	10	1.20	0.03
2	11	1.20	0.03
2	12	1.20	0.03
2	13	1.20	0.03
2	14	1.25	0.08
2	15	1.20	0.03
2	16	1.20	0.03
2	17	1.25	0.08
2	18	1.20	0.03
2	19	1.10	0.07
2	20	1.20	0.03
		Mean = 1.17	$\sqrt{\frac{\Sigma d_2}{n-1}} = 0.052$

[a] $v = (100/C)\sqrt{\Sigma d^2/n-1} = 4.5$

Spectral sensitivity range is sufficient for nearly all conventional analyses, both qualitative and quantitative. Contrast reproducibility is sufficient to provide useful quantitative comparison of intensity ratios between spectra independently exposed and processed. Contrast is reasonably constant with wavelength, allowing wide choice of line pairs. Speed and inertia qualities are favorable.

Resolution is adequate for all ordinary analytical requirements. Analytical precision is indicated to be within ± 5% of the amount of element being determined. The degree of precision obtainable, coupled with the very short film processing time, provides an exceptionally convenient means of recording optical spectra for such applications as (1) survey or type analysis, (2) detection of trace impurities, (3) spectral documentation, and (4) instruction in spectrographic analysis.

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Submitted February 1, 1960

Notes

Carbonyl Frequency and Stability of Some Diphenoquinones

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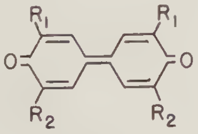
The literature *(1,2)* lists the C=O stretching mode for substances with two quinonoid carbonyls in the same ring between 1660 and 1680 cm^{-1}. The spectra of some 3,3′,5,5′-tetraalkyl-4,4′-diphenoquinones have been recorded and it was found that in such compounds the position of the strongest absorption, and hence what is considered to be the carbonyl band, is 1599 ± 9 cm^{-1}. The band position is apparently insensitive to the effects of physical state, mass, and vibrational coupling because its location is the same in solution and solid spectra as shown in Table I. Diphenoquinone itself has an exceptionally low C=O band (1,2) at about 1630 cm^{-1}, but the alkyl substitution discussed here lowers the value even more.

The infrared instrument used was a Beckman IR-4 equipped with sodium chloride optics and the wavelength calibration was checked before each run with atmospheric water vapor. Thus the band positions are accurate to within ± 3 cm^{-1}. The compounds were made from their corresponding purified parent phenols and are better than 99% pure as judged from melting point and elemental analysis. Further knowledge of electronic and steric effects can be gained from a study of the 2,2′,6,6′-tetrasubstituted diphenoquinones. However, attempts to construct models with this substitution leads one to doubt that compounds of this type can be synthesized since substitution larger than a hydrogen atom in the 2 and 6 positions would produce a tremendous strain in the double bond.

TABLE I. C=O FREQUENCY MAXIMA OF DIPHENOQUINONES IN VARIOUS SOLVENTS[a]

No.	R_1	R_2	*CCl_4 Solution*	*$CHCl_3$ Solution*	*KBr Solid*
I	CH_3	t-C_4H_9	1607 (strong)	1604 (medium)	1606 (weak)
			1593 (weak)	1591 (medium)	1591 (strong)
II	i-C_3H_7	i-C_3H_7	1599	1592	1590
III	i-C_3H_7	t-C_4H_9	1601	1597	1596
IV	t-C_4H_9	t-C_4H_9	1603	1600	1603



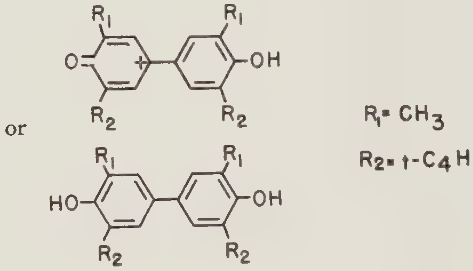
[a] Maxima in cm^{-1}.

It has been reported *(3)* that some of the tetraalkyl substituted diphenoquinones are insoluble in carbon tetrachloride, but this was not observed with these compounds. They were soluble to at least two per cent and gave good intensities in cells of pathlengths from 0.02 to 0.2 mm.

The decrease in the carbonyl frequency can be the result of an increase in the contribution to the structure of quinone resonance forms that require the accomodation of positive charge in the ring. The observed shift is in the expected direction if the prediction is based upon the alkyl substitution, which would increase electron migration toward the ring. Destruction of coplanarity by the presence of groups adjacent to the carbonyl group (ortho-steric effect) would offer a barrier to maximum resonance (conjugation). Thus there would be less contribution from the dipolar forms to the average structure, and this would increase the carbonyl stretching frequency. The similarity of the band positions in the four compounds suggests that increased electron displacement toward the ring and ortho-steric effects coalesce in opposition to each other.

The doublet in I (Table I) is most interesting. The apparent interchange of intensities is probably due to a larger-than-usual shift in the C=O frequency, thus revealing the presence of a weaker C=C mode, but might possibly be caused by enhancement of a C=C stretching mode in the solid phase lattice field.

The quinone with the methyl substituents is the least stable of the compounds studied. A fresh methanol solution of I was yellow in color and the visible spectrum revealed the two quinone bands at 416 and 419 mμ. In about one hr the color had disappeared along with the 419 mμ band, but a new band had appeared at 268 mμ with a shoulder near 285 mμ. Upon the addition of alkali enhancement of the 285 mμ band and the removal of the 268 mμ band occurred. The addition of acid reversed the process and restored this latter band. It thus appears that the new colorless species was of the type



since in such compounds the removal of the proton would cause the enhancement of the 285 mμ band, which is characteristic of the ion. Upon subsequent addition of acid, the reappearance of the 268 mμ band is characteristic of the free acid. The color did not change in the absence of light.

The presence of light did not change the color of IV (Table I), and this suggests that this molecule is the most hindered, probably due to the presence of the tertiary butyl groups.

The authors wish to express their thanks to F. S. Mortimer for assistance in data interpretation, and to F. C. Davis for preparation of the compounds.

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Submitted December 22, 1959

D.C. Arc Analysis. Some Effects of Replacing Graphite with Carbon

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The recent interest in comparing carbon and graphite electrodes has resulted in contributions by Mellichamp and Finnegan *(1,2)* and Allsopp and Shaw *(3)*. Connor and Bass *(4)* have added carbon and graphite powder to the discussion and have considered high voltage a.c. arc excitation. Carbon has been compared with graphite in other situations using the d.c. arc. At times the differences in the behavior of carbon and graphite are appreciable.

In Smith and Mattarella's general semi-quantitative d.c. arc procedure *(5)* (A.S.T.M. E-2 SM 11-2), the sample is mixed with lithium carbonate and graphite and arced for 45 sec. Using 3/16-in. diam., high-purity graphite electrodes (counter electrode, *United* U-1 flat; sample electrode, *National* L-4006), this procedure was compared for porcelain enamel and glass samples using amorphous carbon powder and United UCP conducting graphite (—100 or —200 mesh). The burn was much slower in carbon buffer. Table I illustrates the intensity ratios for a porcelain enamel ground coat. Some of the intensities are greater using graphite and some are greater using carbon buffer. With NBS 91 opal glass all the lines measured were darker using carbon (Table II). In other words replacing graphite buffer with carbon buffer improves the intensities considerably with some types of sample.

While this procedure is not considered to involve burning to completion, the ground coat sample was consumed in 30 sec using graphite buffer and in 60 sec using carbon. Carbon buffer, therefore, has the effect of lowering the temperature at the area of the sample. Tables I and II show that the Li 2741 internal standard line is darker using carbon than graphite, but it should be noted that this line is (reproducibly) self-absorbed and not comparable to the line using graphite.

A total burn method for determining tungstic oxide in titanium oxide was examined (Table III). The experiments consisted of substituting carbon for graphite as crater, counter, and buffer. Table IV shows how carbon craters result in a faster burn, and that carbon buffer slows the burn, but carbon counters were only slightly different from graphite counters.

Table I. Typical Results—Ground Coat

Element	*Line*	*%T Graphite*	*%T Carbon*	*Int. Ratio Graphite*	*Int. Ratio Carbon*
Li	2741	61	28		
Al	2660	72	66	0.88	0.61
Si	2631	70	74	0.90	0.55
B	2496	70	83	0.91	0.48
B	2497	48	62	1.17	0.64
Mn	2794	23	6.8	1.7	1.65
Ni	3101.6	26	35	1.6	0.90
Ca	3179	38	49	1.04	0.75
Na	3303	42	33	1.26	0.92

Table II. Typical Results—NBS 91

Element	*Line*	*%T Graphite*	*%T Carbon*	*Int. Ratio Graphite*	*Int. Ratio Carbon*
Li	2741	66	30		
Al	2660	79	53	0.83	0.75
Si	2631	51	42	1.18	0.85
Si	2506	55	43	1.14	0.83
Ca	3179	31	20	1.55	1.17
Na	3303	58	47	1.10	0.79

Table III. Exposure for Titanium Oxide

D.c. arc; 12 amp
3 mm gap maintained
Exposure; 90 sec
Slit; 50μ
Grating; 4800-6800 A (Second Order)
Primary aperture; 0.5 mm
Neutral filter; 50 % T
Two step filter; 35 % T
Counter electrode; 3/16 in. flat standard grade
Anode; 105-S or L-4006 3/16 in.
Weigh and tamp into electrode: 15 mg (1:2) with graphite
Lines: W 2944.3 A and background, Ti 2874.2 A (unlisted)

Table IV. Titanium Oxide Burn Time[a]

Crater	*Buffer*	*Counter*	*CompleteBurn sec*
G	G	G	90
C	G	G	60
G	C	G	120
G	G	C	75

[a] G—graphite, C—carbon.

Additional combinations of carbon and graphite were tried, adjusting the exposure time to give total burn. Results are summarized in Table V. As before, the burn is faster with carbon craters and slower with carbon buffer. The intensity ratios are higher with carbon craters. Graphite counters resulted in much darker exposures than those produced by carbon counters. Table VI also illustrates this for an impure titanium oxide that was diluted 1:9 with graphite and arced in *National* L-4006 craters.

Further work with rather similar exposures using a porcelain enamel ground coat, G-1 granite, and vanadium pentoxide shows carbon and graphite counters produce nearly indistinguishable spectra.

Summarizing the comparisons between carbon and graphite, the differences have not yet been useful. The only pronounced effect is to lengthen the arcing time requird. Graphite mixes better with most samples. Some samples do not mix with carbon in the *Wig L Bug*, at least not without adding plastic balls. Specifically, the mixing was poor with iron powder, G-1 granite, and porcelain enamel frits, and only fair with tungstic oxide or titanium oxide. The carbon seems to stick to the balance pan, capsule, electrode, and tamp but seems to pack well.

The carbon-graphite electrode comparisons have been summarized elsewhere, except that it has not been reported that carbon counters may reduce the spectral intensity in certain cases.

Table V. Titanium Oxide Exposure Observations

Buffer-Counter-Crater[a]	*Time, Sec*	*Exposure*	*W/Ti Int. Ratio*
C G G	110	Dark	0.40
C G C	80	Dark	0.46
C C G	120	Light	0.52
C C C	80	Dark	0.61
G G G	90	Dark	0.75
G G C	60	Dark	0.83
G C G	90	Light	0.53
G C C	60	Light	0.65

[a] G—graphite, C—carbon.

Table VI. Titanium Oxide 1:9 with Graphite Buffer
Graphite Versus Carbon Counter

Counter	*Per Cent Transmittance*				
	Al 3082	*Ti 2641 I*	*Ti 2945 II*	*Ti 2868.7 II*	*Si 2881*
Graphite	20	40	5.8	41	58
Carbon	60	86	11.7	81	86

The author is glad to express his gratitude to Mr. W. E. Allsopp of the *United Carbon Company*, Bay City, Mich., for supplying the pure carbon powder used.

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Spectroscopic Tricks

A Rotating Platform Assembly

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Following the introduction of the rotating platform for sample excitation a few years ago, at least two such devices are now commercially available for rotating a platform electrode. These mechanisms are supplied with a constant speed motor so that there is no opportunity to nvestigate the effect of speed of rotation upon the results f this is desired.

In a recent investigation on spectrochemical analysis of solutions the author *(1)* studied the rotating platform which was specially designed to give disk rotation from 3 to 30 rpm. The device was constructed by using the motor and gear train of a time switch at quite a cost savings over the available single speed models. This note outlines the construction of a rotating platform assembly. (Figure 1).

A suitable motor was found in a recycling cam timer[*] which could be fitted with a selected gear assembly to give any one of a wide selection of speeds. The micro switch and cam were removed from the timer assembly. Screws at the back of the motor (A) hold it to a base plate (B) which fastens the device to the base of the excitation stand. A U-shaped bracket (C) holds the driven gear (D) in place with the gear assembly (E). A solid micarta rod (F) insulates the high potential from the motor and ground. A brass bushing (G) which fits closely the shaft of the platform holder (H), carries the electrical contact between the electrode clamp and the electrode. A variety of rotational speeds can be obtained by selecting the appropriate gear rack assembly (I), and ten rpm[†] was found satisfactory.

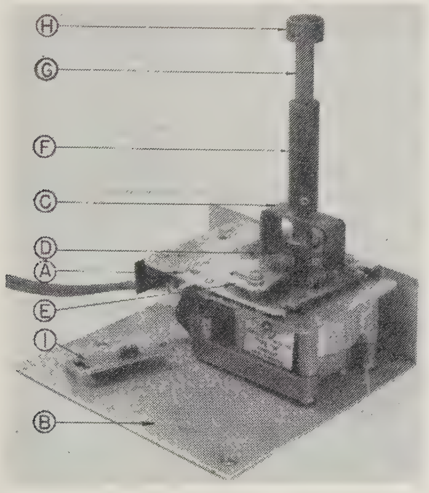

Fig. 1. Rotating Platform Assembly

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Submitted April 19, 1960

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[*] Model CM-O-5W Industrial Timer Corporation, Newark, New Jersey

[†] Gear rack assembly No. B-12, Industrial Timer Corporation, Newark, New Jersey

An Extrusion Method For Supporting X-Ray Powder Camera Specimens

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The advantages of mounting powder specimens free of any binder, adhesives, fibers, or tubes have led several workers to suggest methods and devices for extruding a tiny cylinder of powder. In one of the most recent of these *(1)*, the powder is packed into a 19-gauge stainless steel tube with a plunger made of No. 22 steel wire. A demountable assembly maintains the alignment of anvil, specimen tube, and plunger.

For some time we have been using a simpler version of the method. The powder is packed in an axially drilled brass rod which contains its own loading funnel, and when the specimen has been displaced so that it protrudes 1-2 mm out of the small orifice, the recessed end of the tube is inserted directly into the camera chuck. The mounted specimens are rugged enough, without binder, to withstand any reasonable handling. The plain end of the drill bit used to make the hole provides a suitable plunger for packing and extruding the powder. For convenience in handling, it is mounted in a small plastic handle. The loading of samples is further facilitated by use of a small plastic plate which holds the sample tube upright. A piece of *Plexiglass* (2 in. x 2 in. x ¼ in.) through which an ⅛-in. hole has been drilled, is used.

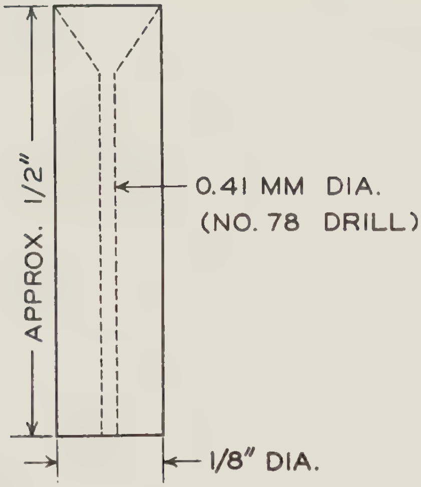

Fig. 1. Extrusion Mold and Specimen Holder

To prepare the specimen for the camera, the drilled rod is placed in the plastic support on a flat, firm surface. The loading funnel is filled with the finely powdered specimen, and the plunger is used to work it down the hole and tamp it. With the powder packed to a depth of 3-4 mm, the tube is lifted out of the holder and the plunger is used to push out the compacted specimen the required distance.

Occasionally and especially with samples which are not easily ground to a sufficiently fine particle size, it is difficult to extrude the packed column. If the specimen should jam in the tube, it can be cleared out by using the cutting end of the drill. Usually it is sufficient merely to reduce the depth of packed material in order to extrude it, and if it is necessary to extend the column, more material may be packed in and pushed forward.

Cleaning of the holder is accomplished easily in the case of organic compounds by immersing it in a suitable solvent and working the drill through the hole several times. Those who work with inorganic and other insoluble specimens may do well to have disposable plastic mounts made up in quantity.

We wish to thank Mr. Jake Kutscher of the Research Area Engineering Shop for his competent performance of a difficult drilling job.

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Submitted April 14, 1960

Novel Cataloging System

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Stock inventory cards* are capable of filling a long-standing need for a simple and inexpensive system for the filing of references, papers and reprints in the spectrographic laboratory. The materials required consist of a number of 8½ in x 11 in stock file cards, a hole punch* and a stacking frame.* Each of these cards has a title line in the upper left corner as well as 7000 numbered squares on its face (Figure 1). This means that a total of 7000 references can be handled by the initial system; in order to expand the system, it is merely necessary to purchase a supply of cards of a different color. In addition, a series of 3 in x 5 in file cards and two filing cases to hold the cards are needed.

The recording process is indicated by the folowing example: Assume that one wants to list the paper by Mohan and Schreiber, "Spectrochemical Analysis of a Nickel Base High Temperature Alloy" (APPLIED SPECTROSCOPY **12**, 6 (1958)). Individual cards are provided with one of the following titles: "Aluminum", "Chromium, "Iron", "Titanium", "Manganese", "Silicon", "Boron", "Nickel Base Alloy", "Atmosphere", "Spark", "Point-to-plane", "Line Pairs", and "Results". These titles represent the points of primary interest and importance of the paper. The paper is now assigned an arbitrary number, e.g. 4371. All of the prepared cards are now placed into the stacking frame and the Square (4371) is punched. This places a hole into the 4371 square of each of the cards involved.

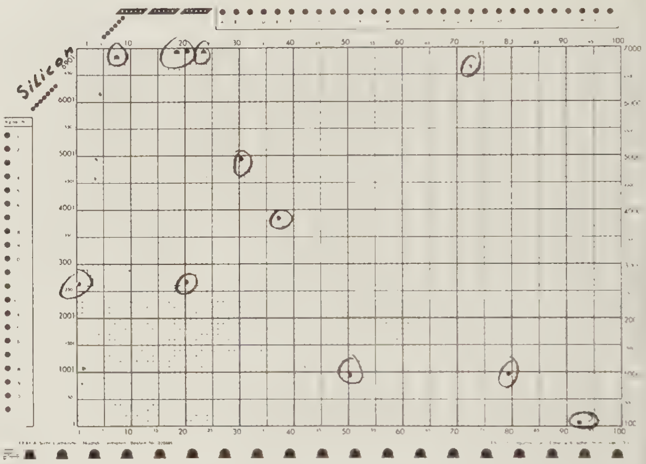

Fig. 1. The "Ekaha" Punch Card
Reference holes are circled

A small card is now marked with the number and provided with the necessary data of the reference. This may be a copy of an abstract, the title cut from the "Bibliography of Recent Papers" from APPLIED SPECTROSCOPY, or some remark as to where the reference may be found. While the abstract cards are filed numerically, the title cards are filed alphabetically for easy access. The title cards are used over and over again for other listings, the "Aluminum" card may be used to file a paper dealing with the determination of aluminum in steel, the "Nickel Alloys" card is used for each additional reference which concerns the determination of any element in Nickel Alloys. Thus each title card is used again and again and gradually accumulates a series of punched holes, which are scattered over its surface (*1*).

On the basis of these cards it becomes possible, in addition to locating references, to answer such questions as:

> To how many papers concerned with Nickel Alloys do I have access?
> (Pull the "Nickel Alloys" card and count the number of holes.)
> Which of these papers provide information on line pairs used?
> (Superimpose the "Line Pairs" card on the "Nickel Alloys" card and count the number of holes still open.)

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What methods have been used for the determination of Boron?
(Pull the "Boron" card and count the number of holes open.)

Thus each punched hole indicates an entry and it also indicates the number of the reference card, which must be checked. Obviously, the more precise the question, the more precise will be the answer. The more cards superimposed upon one another, the fewer the open holes and the easier it is to locate a paper. Many additional questions and particularly combinations of questions may be answered rapidly and easily in this manner. The system, as installed by the author, has found a great deal of use and it has been found to be exceedingly simple to maintain on an up-to-date basis.

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Submitted April 5, 1960

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A Disk Calculator

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Frederickson *(1)* and Goldspiel and Conner *(2)* have described circular calculators for computing intensity ratios and determining composition. One factor discouraging the use of such a calculator is the difficulty in preparing an exact circular two-cycle log scale of sufficient size and accuracy. This problem has been circumvented by the "zerox" (or photostatic) enlargement of the A scale of a 8-in. circular slide rule to a 10-in. diam. The reproduced scale is attached to an aluminum disk, 1/16-in. thick. Relative intensity values for each unit mark of % transmission are tabulated from the customary emulsion Seidel calibration curve. These data are laid out as a circular Seidel % transmission scale on the circumference of a smaller disk 9-in. diam. A special ruler made from rigid transparent plastic is cut so that a radius at the outer end serves as a ruling edge when the two disks and ruler are held concentrically by a bolt, nut, and washer. With the two disks being held together the Seidel % transmission values are marked on the smaller disk at relative intensity positions indicated on the outer log scale.

In use, the ruling edge is replaced by a similar piece of plastic having a ruled mark for an indicator. It has been necessary to prepare one scale for each emulsion lot. The device has proved to be a great time saver and is more convenient to use than the customary calculating boards or conventional linear scales. No originality is claimed for this calculator except the convenience and accuracy of using an enlarged finely divided circular log scale*.

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Resubmitted April 25, 1960

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*Reproductions of the log scale are available from the author upon request.

Working Curve Shifter

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Some laboratories performing a variety of analyses do not find it convenient to prepare working scales for quantitative analysis but prefer to use working curves drawn up as needed or already on file. A curve shifter has been devised and found to be useful for several reasons. Working curves are drawn on conventional log-log co-ordinate paper and traced on to a transparent matte, shifting it horizontally when necessary to avoid confusing overlaps where curves may naturally fall close together. The use of the curve shifter is based on the hypothesis that working curves do not change in slope but may shift in horizontal displacement with changes in working conditions of excitation, photographic processing, or some other factors. Corrections for working curve shifts can be made easily and quickly.

A drawing board (Figure 1) was recessed so that a meter stick or similar rule would slide horizontally near the upper edge and be flush with the top surface of the board. Three ¼-in. dowel pins, about 1-in. long and sharpened in a pencil sharpener, were set into the flat side of the rule about 8-in. apart. A matte finish cellulose acetate sheet, 12-in. x 20-in., 0.005-in. thick*, was punched to fit on the pointed dowel pins and may be easily removed.

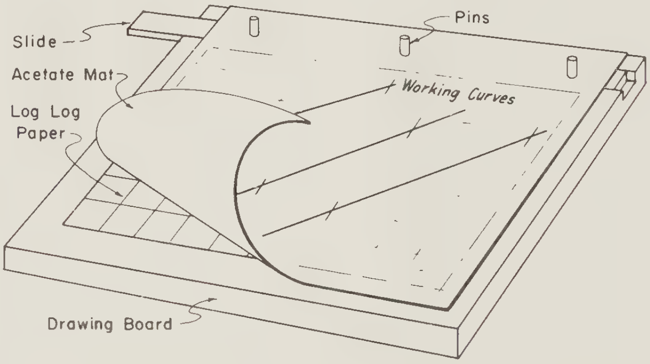

Fig. 1. A Working Curve Shifter

This material may be readily marked by pencil or ink and erased in the same way as tracing paper but is much more durable. In use, working curves are plotted in the customary manner on the usual log-log co-ordinate paper, after which the paper is fastened to the drawing board and overlaid with a piece of Draft Film. The working curves are traced and identified with colored pencils on the matte writing surface of the film, shifting the film sufficiently so that there is no confusion due to overlapping curves. The position of some concentration on the working curve is marked and each curve is identified as it is copied. Also, the position of log intensity ratio = 1.0 is marked on the Draft Film at each end of the concentration axis. One sheet may contain all the working curves for one particular sample type, and a separate sheet may be used for each kind of sample. The graph paper on the drawing board containing the original working curves is replaced by a clean sheet of the same kind of paper positioned vertically so that the log intensity ratio = 1.0 line of the ordinate is exactly under the same mark on the transparent sheet.

A set of working curves superimposed on log-log paper is shown in Figure 1. In use, the curves are set so that the index mark would fall on the indicated concentration, and concentrations read from the intensity ratio values. Alternatively, curve shift may be corrected by placing the working curve on a point determined by an averaged intensity ratio obtained produced by a known concentration of a secondary standard.

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*Material of this type is manufactured by Eugene Dietzgen Co., New York, under the name of Draft-Film No. 157M-5.

This device enables one to make working curve shifts in the same manner that is done with linear scale calculators without laying out the scales or plotting new working curves for each run.

Resubmitted April 25, 1960

A Multiple-Cutting Accessory for Mixing Powders in a Capsule

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When diluting or mixing powders with graphite using the Wig-L-Bug or the Flossy Amalgamator, a very complete mixing is obtained in a much shorter time with the use of a spiral coil of nichrome wire in a disposable gelatin capsule. It has the effect of 20 full-circle cutting edges with each single throw. The wire used is Nichrome Alloy V of 20 mils diam. The spiral coil, in the shape of a cocoon, has 10 complete turns in one in. of length. It is 5/16 in. o.d. at the center and tapers to an ⅛ in. o.d. at the flattened ends. This length causes it to be under slight compression when the disposable No. 000 gelatin capsule is closed, but not enough to have it trap any sample under the 2 points of contact at each end while oscillating. A convenient charge is about 200 mg. Graphite powder does not coat the wire.

Test runs have shown spectrographically no contamination by the wire of graphite or non-corrosive or non-abrasive powders.

Submitted June 24, 1960

Book Reviews

"Advances in Spectroscopy, Vol. I" Edited by H. W. Thompson, Interscience Publishers, New York, 1959, ix + 363 pp., $12.50

This series of "Advances" has gotten off to an auspicious start with the publication of this first volume. The authors are all men who have made significant contributions to the fields they write about and nearly all of the individual articles are more than literature reviews. The main emphasis is on applications of spectroscopy to molecular structure.

Ramsey discusses methods and results of the spectroscopy of polyatomic free radicals (55 pages). Spectroscopy in the vacuum ultraviolet is treated by Price (20 pages). In two short articles of indirect spectroscopic interest, Rank discusses the refractive index of dry air as a function of wavelength, temperature and pressure, and the application of spectroscopy to the determination of the speed of light (14 pages). High resolution Raman Spectroscopy is covered in an excellent article with much experimental and theoretical background by Stoicheff (78 pages). The current status of infrared detectors is reviewed by Moss (35 pages). Elliott presents a number of aspects of the infrared spectroscopy of high polymers (52 pages). A particularly good bibliography of papers in this field accompanies the article. The book ends with a rather detailed review of the application of infrared spectroscopy to the study of rotational isomerism about C-C bonds in saturated molecules by Sheppard (57 pages). This includes a critical examination of the characteristic bending frequencies of C-H bonds in saturated molecules.

E. J. Rosenbaum

"Flames, Their Structure and Temperature" by A. G. Gaydon and H. G. Wolfhard (Second Edition), The Macmillan Co., New York, 1960, 383 pp., $14.00

Being, as it is, one of the more well-thumbed volumes in the physical chemists' combustion library, this book requires only a minimal review in its second edition. However, for the benefit of the neophyte in the combustion field, it is probably worthwhile to describe briefly the first edition published in 1953.

It was the original purpose of this book to supplement the classic combustion books by concentrating on properties specific to standing flames. In this it succeeded most admirably especially with respect to describing techniques and knowledge pertinent to important measurable parameters such as burning velocities and flame temperatures. Included with the latter property was a section on the calculations of flame temperatures, the instructiveness of which was enhanced by an actual example.

In addition, various aspects of flame theory were presented under headings in several categories. The research collected to illustrate a given type of flame was presented under Premixed Flames, Diffusion Flames, etc. Some of the more interesting aspects of flame theory were discussed in chapters on the mechanism of flame propagation, solid carbon in flames and ionization in flames. The distribution of effort in the various areas resulted, apparently, from a reasonable combination of the intensity of research and the authors' interest in those areas.

In this, the second edition, the principal change is the addition of some 200 references which contribute new (since 1953) information in the areas discussed. The references, many from the International Symposia on Combustion, are not merely tacked on, but are carefully and logically molded and incorporated into the text. The bulk of the text itself is unchanged, but numerous paragraphs and pages have been added where warranted by new references, new developments or otherwise.

In general then, this standard volume on flames has been rather smoothly brought up to date. Those who have found it valuable in the past, will find it even more so in the present.

Albert L. Myerson

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